

AD-A056 083

AERODYNE RESEARCH INC BEDFORD MA ADVANCED DEVELOPMENT DIV F/G 14/5  
DEGRADATION TEST MATERIALS.(U)

OCT 77 G M GOLDBERG

F33615-76-C-1179

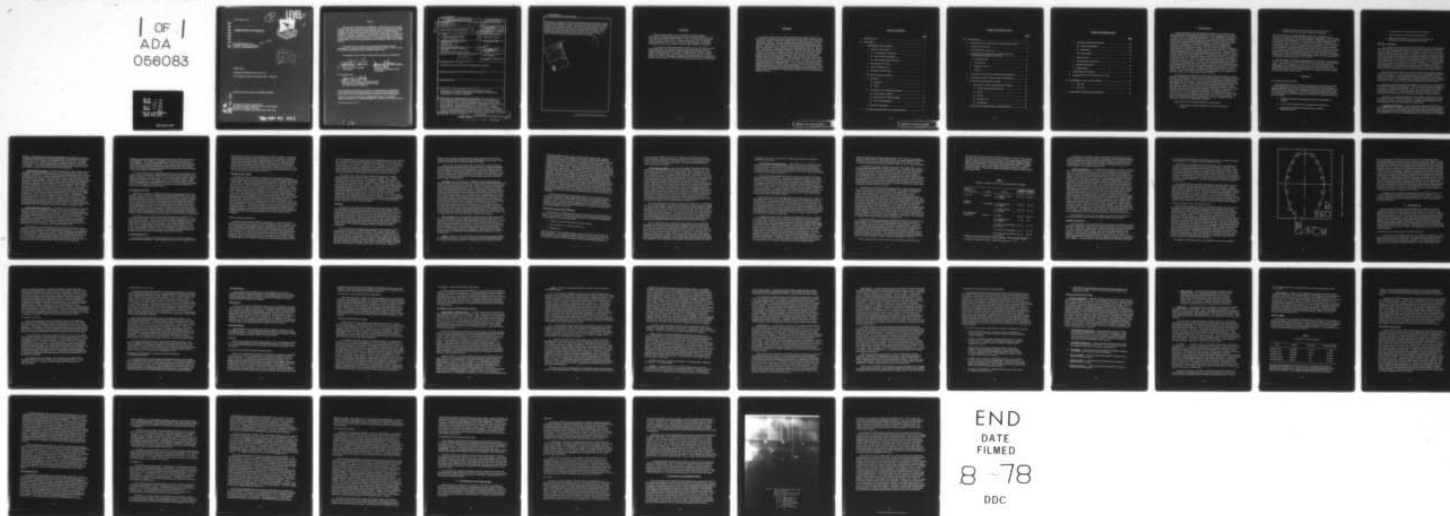
UNCLASSIFIED

ARI-ADD-77-3

AFAL-TR-77-197

NL

1 OF 1  
ADA  
056083

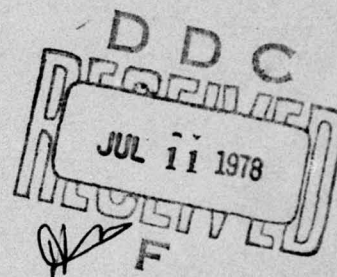


AD A 056083

AFAL-TR-77-197

DEGRADATION TEST MATERIALS

- new*
- ① Aerodyne Research, Inc.  
② Advanced Development Division  
② Bedford, Massachusetts 01730
- 410 744*



October 1977

TECHNICAL REPORT AFAL-TR-77-197

Final Report for Period 24 November 1975 - 1 June 1977

Approved for public release; distribution unlimited

AD No. \_\_\_\_\_  
DDC FILE COPY

AIR FORCE AVIONICS LABORATORY  
AIR FORCE WRIGHT AERONAUTICAL LABORATORIES  
AIR FORCE SYSTEMS COMMAND  
WRIGHT-PATTERSON AIR FORCE BASE, OHIO 45433

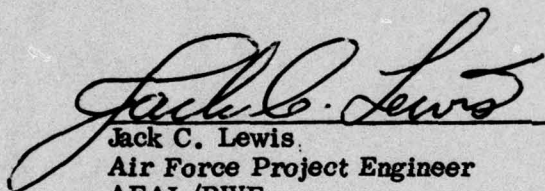
788 007 03 041

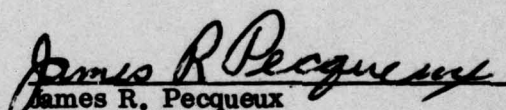
## NOTICE

When Government drawings, specifications, or other data are used for any purpose other than in connection with a definitely related Government procurement operation, the United States Government thereby incurs no responsibility nor any obligation whatsoever; and the fact that the government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data, is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use, or sell any patented invention that may in any way be related thereto.

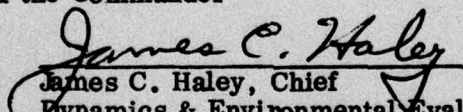
This report has been reviewed by the Information Office (OI) and is releasable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public, including foreign nations.

This technical report has been reviewed and is approved for publication.

  
Jack C. Lewis  
Air Force Project Engineer  
AFAL/RWF

  
James R. Pecqueux  
Technical Manager  
Materials and Processes Group  
AFAL/RWF

For the Commander

  
James C. Haley, Chief  
Dynamics & Environmental Evaluation Branch  
Reconnaissance and Weapon Delivery Division  
Air Force Avionics Laboratory

"If your address has changed, if you wish to be removed from our mailing list, or if the addressee is no longer employed by your organization please notify AFAL/RWF, W-PAFB, OH 45433 to help us maintain a current mailing list".

Copies of this report should not be returned unless return is required by security considerations, contractual obligations, or notice on a specific document.



UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

19 REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM	
1. REPORT NUMBER AFAL-TR-77-197	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER	
4. TITLE (and Subtitle) DEGRADATION TEST MATERIALS	5. TYPE OF REPORT & PERIOD COVERED FINAL REPORT 24 November 1975 - 1 June 1977		
7. AUTHOR DR. GERSHON M. GOLDBERG	6. PERFORMING ORG. REPORT NUMBER ARI-ADD-77-3		
9. PERFORMING ORGANIZATION NAME AND ADDRESS AERODYNE RESEARCH, INC. CROSBY DRIVE BEDFORD, MA. 01730	8. CONTRACT OR GRANT NUMBER(s) F33615-76-C-1179		
11. CONTROLLING OFFICE NAME AND ADDRESS AIR FORCE AVIONICS LABORATORY AFAL/RWF WRIGHT-PATTERSON AFB, OH 45433	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS USAF0051		
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)	12. REPORT DATE 15 OCTOBER 1977		
	13. NUMBER OF PAGES 40		
	15. SECURITY CLASS. (of this report) UNCLASSIFIED		
	15a. DECLASSIFICATION/DOWNGRADING SCHEDULE		
16. DISTRIBUTION STATEMENT (of this Report) APPROVED FOR PUBLIC RELEASE, DISTRIBUTION UNLIMITED			
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)			
18. SUPPLEMENTARY NOTES			
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) DEGRADATION TEST MATERIALS (DTM), PHOTOGRAPHIC FILMS, PHOTOGRAPHIC CAMERAS, PHOTOGRAPHIC PRINTERS, PHOTOGRAPHIC PROCESSORS, SCRATCHES, ABRASIONS			
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Two materials have been developed for testing of film transport mechanisms to detect malfunctions likely to damage photographic films. One material is intended for dry applications only, the other for applications where there is contact with aqueous solutions. The designations *wet* and *dry* degradation test material (DTM) have been applied to differentiate between the two. The dry DTM, a coating of solvent-filled microcapsules in a gelatin/polyvinyl alcohol matrix on a black base, produces a contrasting white mark at the site of a scratch or abrasion. The wet DTM, a coating of empty microcapsules in a similar matrix, has a white surface covering			

DD FORM 1 JAN 73 1473

EDITION OF 1 NOV 65 IS OBSOLETE

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

410744 38 07 03 0411 1



UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE(When Data Entered)

the black base. Damage to this DTM causes localized removal of the white coating to reveal the black background. Versions of both DTMs have been produced on a flashed, processed Estar-based film substrate. The major part of the program described in this report was an attempt to provide a wet DTM on a dyed black polyester substrate. Satisfactory results were not obtained because coatings either lost much of their contrast after contacting aqueous solutions or had poor wet rub resistance. Formulations having good wet rub resistance showed excessive contrast loss while formulations retaining their contrast had poor wet rub resistance.

ACCESSION for

NTIS

DDC

UNANNOUNCED

JUSTIFICATION

White Section ☒

Buff Section ☐

BY DISPOSITION/AVAILABILITY CODES

SPECIAL

A

SECURITY CLASSIFICATION OF THIS PAGE(When Data Entered)

## FOREWORD

This report (ARI-ADD-77-3) was prepared by Aerodyne Research, Incorporated, Bedford, Massachusetts on Air Force Contract F33615-76-C-1179. The contract was initiated under Project No. 0051. The work was administered under the direction of the Air Force Avionics Laboratory, AFSC Aeronautical Systems Division, with Mr. Jack C. Lewis as Project Engineer. The studies presented here began on 24 November 1975 and were concluded on 1 June 1977.

Dr. Gershon M. Goldberg was Project Director for this contract and carried out the majority of the microencapsulation and subcoating studies. Miss Ann McNally performed the laboratory scale subcoating and DTM coating as well as testing of DTM properties. Mr. Richard J. Starble and Mr. Vincent F. Bilotta handled the setting up of the coating machine under the direction of Mr. Burton D. Figler. Mr. David E. Willoughby contributed to both the chemistry and machine set-up phases of the program. This report was submitted by the author on 28 July 1977.

### SUMMARY

An effort has been made to develop a degradation test material (DTM), a non-photosensitive coating on a polyester substrate that can be used as a simulated film to test film transport systems for imperfections or malfunctions likely to damage a photographic emulsion. No single coating was found capable of functioning in air and in the variety of aqueous environments presented by a photographic processing machine. Accordingly, two versions of DTM were developed, one for dry and one for wet applications. Both were based on microencapsulation technology. The dry DTM, a transparent microcapsule coating on a black base, produces a contrasting white mark at the site of a scratch or abrasion. The wet DTM, an opaque coating of empty microcapsules on a black base, allows black to show through the white coating where the coating has been damaged. Both materials were provided on flashed, processed Estar-based film. Testing indicated that the dry DTM worked well but the wet DTM was lacking in wet rub resistance. The major portion of the program was directed toward the production of a wet DTM with improved properties on a dyed polyethylene terephthalate base. The two major problems encountered, inadequate bonding to the substrate and loss of opacity of the coating after passage through aqueous solution, could be solved individually but not simultaneously. Formulations that bonded strongly to the base suffered almost total loss of opacity after wetting while formulations that retained opacity well could be easily rubbed from the substrate when wet.



## TABLE OF CONTENTS

	<u>Page</u>
I INTRODUCTION .....	1
II DISCUSSION .....	2
1. PROCESSED FILM SUBSTRATE .....	2
a. Selection of Approaches .....	3
(1) Formaldehyde Overcoating .....	3
(2) Free Solvent Minimization .....	4
(3) Factors Influencing Repellencies .....	4
b. Overcoating of Dry DTM .....	5
c. Control of Repellencies .....	5
d. Evaluation of Test Coating .....	6
2. DYED POLYESTER SUBSTRATE .....	6
a. Subcoating .....	7
(1) Polymeric .....	8
(2) Gelatin .....	8
b. Formulation of Microcapsule Suspension .....	9
(1) Improvement of Adhesion .....	10
(2) Improvement of Opacity Retention .....	11
(3) Control of Repellencies .....	14
c. Alternative Approaches .....	14
3. COATING MACHINE SETUP AND MODIFICATION .....	15

## TABLE OF CONTENTS (Contd.)

	<u>Page</u>
III EXPERIMENTAL .....	17
1. PREPARATION OF MICROCAPSULE COATING SOLUTION .....	17
2. COATING OF WET DTM .....	18
3. OVERCOATING OF DRY DTM .....	19
4. ATTEMPTED PREPARATION OF MICROCAPSULES CONTAINING LOW BOILING SOLVENTS .....	19
a. Tetramethylsilane .....	20
b. Ethyl Bromide .....	20
c. Methylene Chloride .....	20
d. Freon TF .....	20
5. ALTERNATE ATTEMPT TO REMOVE FREE SOLVENT .....	20
6. ATTEMPTED IN-SITU MICROCAPSULE FORMATION .....	21
7. ALTERNATIVE SUBSTRATE STUDIES .....	21
a. Subcoatings for Glossy and Matte Black Polyester .....	22
(1) Styrene/Maleic Anhydride (S/MA) .....	22
(2) Gelatin .....	23
(3) Photozid .....	24
(4) Carboset XL-19 .....	25
(5) Miscellaneous .....	26
8. VARIATIONS ON MICROCAPSULE PREPARATIONS .....	27

## TABLE OF CONTENTS (Contd)

	<u>Page</u>
a. Lowering of Capsule Wall Porosity .....	28
(1) Polymer Incorporation .....	28
(2) Thixotropes .....	29
(3) Cross Linkers .....	30
b. Binder Variation .....	30
c. Stoichiometric Preparations .....	31
d. Waterproofing Agents .....	32
e. Miscellaneous .....	33
9. COMPATIBILITY STUDIES .....	35
10. PREPARATION AND COATING OF DRY DTM .....	36
IV PROPERTIES OF THE DTM COATINGS .....	36
a. DRY DTM .....	37
b. WET DTM .....	37
V CONCLUSIONS AND RECOMMENDATIONS .....	38



## I INTRODUCTION

Current methods for assessing damage to roll film caused by physical handling and transport through equipment such as processors, duplicators, and various evaluation devices, are generally unsatisfactory. As a consequence on Contract No. AF 33615-74-C-1151 a search was initiated for a material that would simulate the properties of film yet indicate damage close to the source with sufficient contrast that the defect produced could be readily detected. On Phase I of that contract two versions of a degradation test material (DTM) based on microencapsulation technology were generated, one for dry applications and one for applications involving contact with aqueous solutions. The "dry" DTM consisted of a coating of solvent-filled microcapsules on a flashed, processed Estar-based film. The capsules, being transparent, did not alter the black appearance of the film. Breakage of the capsules released the solvent, which evaporated rapidly from the surface of the film, to leave a white track in the damaged area. The contrast between the white mark and the black background was high enough that the mark could be seen from a distance of several feet. The "wet" DTM was a coating of predominantly empty microcapsules on the same substrate. The microcapsules acted as light scattering centers and gave the surface a white appearance. Fracture of the capsules allowed the black background to show through the white outer coating. The contrast between the black mark and the white background was not as sharply delineated as the dry DTM's white mark on black background. However, the mark could readily be seen from a foot away. A Phase II effort was successful in producing a few thousand feet of the dry DTM for delivery. The wet DTM posed more difficult coating problems and the quality of the material obtained was not high enough to warrant testing.

The complexity of coating the wet DTM arose from the need to apply an under-coating of formaldehyde in gelatin to secure adequate bonding to the flashed, processed film used as the substrate. For best results the DTM coating had to be applied before this intermediate layer was dry. Since a much lower defect level was noted when the intermediate layer was omitted, it appeared that an incompatibility existed between the two coatings. A review of the factors involved in coating the wet DTM led to the conclusion that there were three potential sources of this incompatibility, the formaldehyde, free organic solvent in the microcapsule suspension, or the hardened nature of the processed emulsion on the Estar substrate. Accordingly, Contract No. AF 33615-76-C-1179 was initiated to examine ways of controlling these factors in order to provide wet DTM coatings of good quality. By improving the method of applying the formaldehyde layer and increasing the viscosity of the DTM suspension, the defect level of wet DTM coatings was minimized and a 125 ft. length of 6.6 inch material was delivered for preliminary evaluations.

Testing of the wet DTM sample indicated two shortcomings:

1. The coating was not held strongly by the substrate in the edge region.

2. Contact of ribbed rollers of the processor with the DTM left a roller pattern and decreased the opacity of the coating.

The first of these was a machine limitation, the second was believed to be a consequence of the fact that the DTM layer itself was not hardened. At this point the program was expanded and its aims were broadened. Additional funding was supplied for the purchase and installation of a coating machine capable of handling a wide enough web to provide 9-1/2 inch DTM. Since the use of flashed, processed film as the substrate is not cost effective, the decision was also made to go to a black dyed polyester substrate. As the experimental work progressed, two major problems were encountered; bonding of the DTM coating to the substrate was not strong enough for the coating to resist rubbing while in the wet state, and the coating lost much of its opacity in solution. While modifications could be made on either of these properties, both could not be improved simultaneously. At the completion of the proposed experimental program the wet DTM did not exhibit enough of the desired properties to warrant the coating and delivery of test material.

This final report documents the experimental work conducted on both portions of Contract No. F33615-76-C-1179 and summarizes the current status of wet DTM technology. Also, since Contract No. F33615-74-C-1151 had no formal reporting requirements, the preparation and coating of the dry DTM are described in the experimental section. The properties of the most representative wet and dry DTM materials prepared to date are presented along with an estimate of the development work needed to perfect each version.

## II DISCUSSION

### PROCESSED FILM SUBSTRATE

In the initial phase of this work the three most likely causes of the poor quality wet DTM coatings were assumed to be incompatibility between the formaldehyde-containing interlayer and the DTM suspension, the presence of free (unencapsulated) solvent in the DTM suspension, or the hardened nature of the emulsion layer on the SO-192 film used as the substrate. A list of six potential approaches for remedying these conditions was considered and three were selected for experimental follow-up. The list included:

1. Altering the sequence of applying the DTM and the formaldehyde coatings.
2. Use of a lower boiling solvent in preparing the microcapsules.
3. Evaluation of formaldehyde preparations from different industrial sources.

4. Use of gelatin cross-linkers other than formaldehyde.
5. Coating on films processed in non-hardening fixer.
6. Softening of the gelatin on the processed Estar-based film by chemical or enzyme treatment prior to coating.

#### Selection of Approaches

The rationale for choosing the first three approaches was that they represented the smallest perturbation from the previous work and would therefore be easiest to carry out. The fourth approach would be a logical one to follow if it were certain that formaldehyde was the cause of the incompatibility. However, some of the first coatings of wet DTM made on the previous contract showed only minor defect levels despite the presence of formaldehyde. On this basis it appeared worthwhile to check out the formaldehyde thoroughly before abandoning it for other cross-linkers. The fifth approach could not be carried out at Aerodyne Research since all of the flashed, processed film used on the program was government furnished. The sixth approach, if required, would be most difficult to carry out on a routine basis. Chemical or enzyme degradation of a material such as gelatin cannot be readily controlled. A better alternative, and that which was ultimately followed, was to depart completely from the use of finished film and go to a properly subcoated polyester substrate.

Reversing the order of application of the wet DTM and formaldehyde coatings was given first priority for study since this did not involve changing any of the operations prior to coating. It had the advantage that the microcapsule layer could be coated and dried before the formaldehyde was applied and there was no necessity for coating "wet on wet". Formaldehyde should be capable of penetrating the unhardened gelatin of the DTM coating and diffusing to the base layer to form cross-links.

The use of a low-boiling solvent in forming the microcapsules was designed to eliminate the eventuality that free organic solvent in the microcapsule suspension was responsible for coating incompatibilities. After the capsules are formed, heating of the aqueous suspension above the boiling point of the solvent should boil away any unencapsulated material. (Capsules containing solvent can usually be heated to temperatures somewhat above the boiling point of that solvent without rupturing).

The reason for evaluating formaldehyde from different manufacturers was that this compound is quite reactive and undergoes oxidation and condensation reactions under mild conditions. Therefore there was a possibility that contaminants in the formaldehyde contributed to the observed incompatibilities.

Formaldehyde Overcoating - As the experimental program progressed there were indications that the three approaches selected for study did not provide answers to all of the problems. Reversing the order of putting down the DTM and formaldehyde coatings improved the cosmetic appearance of the final product in that the gross incompatibilities, which gave a patterned appearance to the coating, were eliminated.



However, a large number of small circular repellency spots remained. If the formaldehyde overcoating solution contained enough gelatin, it coated fairly smoothly over the DTM layer but did not provide an adequate bond to the substrate. If the gelatin content was lowered, bonding was good but the coating lost some of its desirable characteristics. The aqueous formaldehyde overcoating lowered the contrast of the DTM coating. Then, when additional contrast was lost in going through the processing solutions, scratches and abrasions were poorly delineated.

Free Solvent Minimization - Attempts to substitute low boiling organic solvents for cumene in the microencapsulation process met with little success. Most of the available low boiling solvents did not dissolve enough terephthaloyl chloride to provide an adequate capsule wall. Reaction temperatures had to be controlled closely or the heat generated by the interfacial polycondensation reaction tended to boil the solvent and cause excessive foaming. Scale-up of such a reaction would have presented severe difficulties. Minimization of the problem of free organic solvent was accomplished by a different approach. The ultrasonic probe used to emulsify the organic phase into the aqueous gelatin exerts its action in a downward direction. Since, in the case of cumene, a thin layer of organic solvent floats on the surface of a much larger volume of aqueous phase, placement of the probe in the aqueous layer does not draw the solvent into this phase. On the other hand, placement of the probe in the organic layer does not force this lighter phase into the heavier aqueous phase with any degree of efficiency. Thus an improved mixing method was needed. A combination of physical, mechanical, and sonic techniques was used to achieve this end. Mixing of the cumene with small amounts of solvents considerably denser than water to bring the overall density to 1.0 and stirring with a magnetic stirrer bar dispersed the organic liquid well enough that, when the probe was turned on, a uniform distribution of cumene droplets was emulsified into the aqueous gelatin. When these droplets were encapsulated there was no visible evidence of free solvent in the aqueous phase.

Factors Influencing Repellencies - Elimination of free solvent from the aqueous phase did not lower the frequency of repellency spots in the DTM coating. A hand coating of barium sulfate in gelatin was made as a control to determine whether some component of the microcapsule system was at fault. When this coating was also found to be full of repellency spots, the gelatin stocks were next tested for possible contamination. All of the gelatins used were first made up as 10% or 15% solutions and aliquots of these solutions were diluted to provide the gelatin concentrations needed in each operation. A hand coating of 10% gelatin on the processed Estar-based film proved to be defect free. However, after dilution of the solution to a 5% gelatin level, coatings were found to have several repellency spots.

Experiments on pieces of the processed SO-192 used as the substrate on the initial phase of this program indicated that the repellencies arose, in part, from this material. Samples immersed in water and withdrawn emerged with what appeared to be a continuous film of water on their surface. Almost immediately the film broke in a number of areas to reveal circular portions of substrate that did not seem to be wet. The addition of wetting agents to the water did not alter the behavior of the SO-192. We had previously noted that, during machine coating of the DTM, the coating solution seemed to cover the substrate evenly at the point of application.

Repellency spots did not begin to appear until the film had traveled a few feet from the coating head. This behavior, if anything, was worsened in the presence of wetting agents. The strong parallel between the two sets of observations led us to conclude that the important characteristic of the coating solution was its viscosity. The solution being coated flowed readily and tended to flow around the repellent areas. The addition of wetting agents rendered the solution even more fluid so that it flowed more rapidly around these areas.

The relative freedom from repellencies of the dry DTM which, although coated on the same SO-192 substrate, contains at least 5% gelatin, lent confirmation to our tentative conclusion. However, it was not possible to increase the gelatin content of either the formaldehyde coating solution or the wet DTM coating solution. Gelatin solutions with much over a 2.5% gelatin content cross-linked too rapidly with the amount of formaldehyde required and tended to set up in the lines feeding the coating head. The DTM solutions, when made up to gelatin concentrations higher than 2.5%, gave very poor contrast (gray against black).

#### Overcoating of Dry DTM

At this point we looked in a different direction for potential improvement of the wet DTM. The dry DTM shows relatively good coating characteristics and provides excellent contrast. However, it does not bond well enough to the substrate to resist the action of aqueous solutions. It also tends to become opaque in contact with water. If the dry DTM could be overcoated with a thin layer of water impervious polymer from an organic solvent solution, its properties should not be influenced by immersion in water unless a scratch or abrasion disturbs the overcoating. While such an overcoating might be expected to lower the sensitivity of the dry DTM, the DTM is currently more sensitive to overall pressure, scratches, and abrasions than the films which it is expected to simulate. Therefore, while continuing to seek improvements in the wet DTM coating formulations, we also looked at the possibility of using the dry DTM as a basis for a material that could be employed in both wet and dry environments.

Overcoating of the dry DTM showed promise of being a viable approach. The overcoating reduced the sensitivity of the DTM and delayed the appearance of scratch marks for a few seconds. (The solvent liberated by capsule breakage required some time to diffuse through the overlying polymer). Water did not penetrate the overcoating but, at the same time, the overcoating was not readily damaged in the wet state. The wet organic surface behaved like a lubricant film and the stylus of the scratch tester seemed to slide across it. This drawback can probably be overcome by the use of alternative polymers. However, the approach was shelved when substantial progress was made on the original version of the wet DTM.

#### Control of Repellencies

The problem of applying the formaldehyde undercoat was solved by turning to a different method of application. Methanol appeared to wet the SO-192 surface evenly.

When about 20% of aqueous 37% formaldehyde was added to methanol, the resulting solution retained the good wetting characteristics of pure methanol. It contained enough water to swell the gelatin of the photographic emulsion without leaving the surface in a wet condition when the methanol evaporated. Increasing the gelatin content of the DTM coating solution without losing contrast was accomplished by doubling the concentration of organic phase initially emulsified into the aqueous gelatin so that the microcapsule concentration per unit volume was doubled. It was then possible to add an equal volume of concentrated gelatin solution and achieve full contrast with gelatin concentrations as high as 8%.

#### Evaluation of Test Coating

The final wet DTM was prepared by applying the methanolic formaldehyde solution through a wick at the first coating station and overcoating the swollen gelatin of the substrate with a microcapsule suspension containing 5.5% gelatin at the second coating station. Although this coating was not totally free of repellency spots, those present were quite small in diameter and their frequency was less than 5% of that observed on any previous wet DTM coating. When this test coating was run through a processing machine some loss of material was observed in the edge regions and the ribbed rollers of the machine left a pattern which strongly reduced the opacity of the DTM. The edge problem was not unexpected. In conventional coating operations it is common to coat wider than desired and slit away both edge regions since there is likely to be a fall-off in thickness and properties in these areas. The coating machine available at the beginning of the program could only apply material across a 5-3/4 inch web width. Since the DTM was provided in a 6.6 inch wide format, it was impossible to trim the edges to eliminate nonuniformities. At the time the test coating was prepared there was a possibility that the "wet" DTM could serve both for wet and dry applications. Therefore, no attempt was made to put hardeners in the actual DTM layer because it was felt that this would reduce the scratch sensitivity of the material for dry use. It thus appeared that the combination of a coating apparatus capable of handling a wider web, a substrate other than SO-192 film, and some minor modifications in the DTM formulation would lead to a product with the desired properties.

#### DYED POLYESTER SUBSTRATE

A coating machine with the capability of handling an 11-1/2 inch web became available as a result of the phase out of certain operations by Itek Corporation. This was purchased with contract funding, moved to suitable space in the Aerodyne building, and refurbished and modified to adapt it to the coating of "wet" DTM. At the same time the decision was made to switch to dyed black polyethylene terephthalate as the substrate. For production purposes the use of flashed, processed film would not be cost effective. In the first place, the film would have to be purchased thus making the cost of the DTM greater than the cost of film even if no other costs were involved. However, the film would also have to be flashed and processed. Ideally, a substrate width of 11-1/2 inches is required since webs cannot be coated out to the



very edge (solution would get onto the back and contaminate the rollers of the machine) and, as mentioned before, the edge regions of the coating should be cut away since they are likely to be nonuniform. Machines for processing 11-1/2 inch webs are not common and this, too, would be an expensive step. In addition, the DTM would have a silver content and, after use, would need to be submitted for silver recovery. Silver as the source of the black background is not ideal, since passage of the wet DTM through color processing solutions would result in removal of silver by the bleach and fixing steps. Dyed polyester is inert to color processing solutions.

The primary dyer of polyester film, Martin Processing, Inc., initially provided samples of three types of material, a glossy surfaced film, a matte surfaced film and a film subcoated to accept lacquer coatings. Screening tests indicated that the subcoated film had some affinity for formaldehyde which, in turn, could bind the microcapsule coating. However, when an order was placed for the dyed, subcoated polyester, we were told that, as a result of severe blocking problems arising after reaction of the hot dye solution with the subcoating layer, Martin had discontinued production of this material. Of the two remaining choices the matte surfaced film appeared preferable since it would be necessary to subcoat the polyester and the matte would provide some "tooth" for holding the subcoating. Unfortunately, the matte surface film was available only in 2, 3 or 5 mil thickness whereas the films we wished to simulate were on 4 mil Estar. As a result, quantities of both 3 mil matte surfaced film and 4 mil glossy surfaced film were purchased and used for the remainder of the experimental program. The 3 mil matte material actually measured 3.5 mils on an Ames gauge.

#### Subcoating

At this point subcoating of the dyed polyester became the primary problem. Since the dyeing process involved contact of the polyester with an organic solvent solution of dye at a temperature high enough to soften its surface, the dye is actually incorporated into the film surface. In the case of the matte material, a filler is included while making the polyester film so that, after dyeing, the surface has both dye and filler incorporated. Thus, the surface characteristics of both available substrates were not the same as might be expected from a "pure" polyester such as Estar. As the experimental work progressed it became apparent that a gelatin matrix containing a high concentration of microcapsules does not behave as gelatin normally would. Thus the task of finding a suitable subcoating was further complicated.

The dyed polyester as purchased had a completely water repellent surface. A piece immersed in water and removed shed the water as large droplets almost instantly after it cleared the water/air interface. The affinity of the polyester for water could be improved by physical or chemical methods. Roughening of the substrate by sandblasting or subjecting it to a corona discharge changed it enough that, after wetting, the water filmed out over the surface. Chlorinated solvents such as methylene chloride, chloroform, ethylene dichloride and trichloroethylene extracted dye from the polyester as did acetone, ethyl acetate, dimethyl formamide, dimethyl sulfoxide, dichloroacetic and trichloroacetic acids, and m-cresol. Methylene

chloride was by far the most potent solvent in this respect since not only was it capable of removing the dye totally from the substrate after a long enough contact period (2 hours) but it also caused the substrate to shrivel.

In the course of the subcoating studies several avenues were investigated. Polymers known from published work to adhere strongly to polyethylene terephthalate were applied from the recommended solvents, polymers having substituents that could interact with gelatin were applied from solvents that released dye from the film surface, "dopes" containing polymers and gelatin were coated from various solvents, and gelatin was applied directly from solutions in solvents that attacked polyester, or from water-in-solvent or solvent-in-water emulsions in which the aqueous phase contained gelatin.

Polymeric - Of all the materials investigated a styrene/maleic anhydride copolymer (S/MA) gave the best results. It could be coated from acetone solution and dried to a smooth, even layer that could not be lifted from the base with Scotch tape. At this stage the subcoating did not wet well. However, if treated with an alkaline solution the maleic anhydride residues were hydrolyzed and the ionized carboxyl groups of the polymer promoted even wetting. Unfortunately, conversion of the subcoating to a water-wettable state loosened the bond to the base and the layer could then be lifted by Scotch tape. This complication could be controlled in one of three ways. Smooth gelatin coatings could be made on the non-wetting anhydride form of the polymer by employing a wetting agent in the water solution. Hydrolysis of the anhydride during drying of the gelatin coating apparently proceeded in a different manner than did the prehydrolysis with alkali. Alternatively, the inclusion of other more hydrophobic polymers such as Bakelite VMCA (a terpolymer of vinyl chloride, vinyl acetate and maleic acid containing only 2% by weight of the acid) in the subcoating solution allowed hydrolysis without loosening the bond to the base. Interaction of the S/MA with a high molecular weight amine such as Hercules Amine D, which should cause opening of the anhydride and formation of an amide from one of the carboxyls (thus halving the number of carboxyl groups free to form salts), also prevented loosening of the subcoating without lowering the wettability.

Either gelatin alone or a photographic emulsion could be coated over the modified S/MA subcoatings to form a tightly held layer that withstood hot water from a sink spray and a full processing cycle (development, wash, fix, wash, dry). The wet gelatin layer, after emerging from hot water, could be rubbed vigorously with a thumb without being removed or displaced. However, the microcapsule coating did not bond strongly to the S/MA layer until the processing cycle was completed. The hardener contained in the fixer (most probably alum) apparently linked carboxyl groups from the hydrolyzed polymer to the gelatin. At any stage prior to fixation, brushing of the wet coating lightly with a finger resulted in removal of the microcapsule layer.

Gelatin - Gelatin was found to be soluble in at least three solvents that attacked the dyed polyester surface. Solutions were prepared by dissolving gelatin directly in m-cresol or in dichloroacetic acid. Trichloroacetic acid, since it is a solid,

required the addition of a few drops of water to form a liquid matrix capable of dissolving gelatin. The dichloroacetic acid solution coated on black polyester produced a film which, when rinsed free of acid and dried at 90°, curled badly and would have been difficult to handle for any subsequent coating application. The solution of gelatin in m-cresol was not coated directly on the substrate. Instead, droplets of this solution were dispersed in methylene chloride and the substrate was coated from the latter solvent. The gelatin subcoating prepared in this way did not bond directly to other gelatin. If a formaldehyde solution was coated on the subcoating immediately before applying the DTM suspension, the resulting film turned pink on drying. The bond to the substrate surface, while initially appearing adequate, was weakened by photographic processing; on subsequent drying, the processed area lifted from the base. Gelatin applied to the base from trichloroacetic acid, then washed to remove the acid and dried, formed a tenacious coating that dried with a whitish cast. In contrast to the dichloroacetic acid, the trichloroacetic acid did not cause the black polyester to curl. This subcoating, when wet with formaldehyde and overcoated with a microcapsule suspension, formed a DTM that was lacking in wet rub resistance. However, when black polyester subcoated with gelatin from trichloroacetic acid was overcoated with an acetone solution of S/MA (a step that released dye from the substrate) and dried, the resulting subcoating could be wet with formaldehyde and coated with a microcapsule suspension to give a DTM with good wet rub resistance.

An alternative method of applying gelatin directly to the dyed polyester substrate was to emulsify a gelatin solution into a solvent such as methylene chloride or conversely to emulsify a solvent capable of attacking the substrate into a gelatin solution. Coatings of these emulsions, when dry, could not be lifted from the base with Scotch tape. On wetting with formaldehyde and overcoating with a microcapsule suspension, the gelatin subcoat was loosened and did not provide a bond that would withstand photographic processing.

#### Formulation of Microcapsule Suspension

The procedure for preparing a microcapsule suspension that contained sufficient binder to hold it on a substrate had been worked out while improving the coating of the DTM on processed film. The three problems that had to be addressed on changing to dyed polyester for the base material were:

1. Adhesion of the microcapsule layer to the subcoating.
2. Loss of opacity on processing of the DTM.
3. Repellencies.

Each of these had to be unequivocally solved in order to provide a wet DTM with the desired properties. The repellency problem proved to be the easiest to control; the other problems, though individually soluble, could not be solved simultaneously. The microcapsule suspension could be formulated to have improved adhesion but such



blends invariably exhibited a severe loss of opacity. On the other hand, microcapsule suspensions that retained a major portion of their opacity did not generally adhere well to the subcoating. Unfortunately, there are so many parameters that can be varied that it was impossible to carry out all of the possible experiments within the scope of the program.

Improvement of Adhesion - The S/MA subcoating on the dyed polyester was shown to be compatible with both gelatin and a photographic emulsion. It held the gelatin tightly even without the aid of formaldehyde or other cross-linkers. Since the microcapsules were in a primarily gelatin matrix, the matrix itself should not have contributed to the lack of adhesion of the DTM layer. Examination of the composition of the microcapsule suspension indicated that free cumene or the polyamines (which are present in excess) are possible suspects. Cumene is water insoluble and would interfere in an aqueous coating system whereas the polyamines would be reactive toward formaldehyde and might lower the efficiency of cross-linking of the gelatin. Minimization of the effects of these chemicals was attempted by separating them from the suspension, by increasing the amount of acid chloride to the level where it would consume all of the polyamines, and by incorporating additives that would restrict the mobility of cumene from the capsules. In addition, attempts were made to increase the water resistance of the binder by using mixtures of polyvinyl alcohol (which conferred better film forming properties on the DTM coating) with the gelatin and by incorporating cross-linkers such as alum and chrome alum which might better be expected to interact with the carboxyls generated in the S/MA. In other experiments gelatin layers coated under or over the S/MA layer were utilized in an attempt to make a more compatible gelatin to gelatin bond.

All of the experiments only affected the adhesion in minor ways. Incorporation of various reactive additives in the S/MA subcoating was tried as a means for linking the coatings more strongly. Substances such as cyanuric chloride, epoxides, silane adhesion promoters, colloidal silica, and colloidal titania were used unsuccessfully. The ability of hardening fixer to improve the wet rub resistance was used as the basis for another line of experimentation. The acid hardener solution for Kodak Rapid Fix is packaged separately and attempts were made to incorporate some of this solution in the microcapsule suspension or to thicken it and coat it as an intermediate layer. In all cases it hardened the gelatin layer and improved the film strength but did not promote better adhesion between the subcoating and the microcapsule coating.

The best adhesion and wet rub resistance was obtained from a microcapsule preparation in which the waterproofing agent 3-heptafluoroisopropoxypropyltrichlorosilane was incorporated in the cumene in an attempt to waterproof the capsule pores and prevent water from diffusing into the empty capsules. Coatings from this preparation on S/MA subcoated black polyester could be rubbed, when wet with water alone or with processing solutions, without loss of material. Unfortunately, this particular additive led to a coating that lost its opacity totally after cycling through photographic processing solutions. In its presence other additives which, when used alone in microcapsule preparations, gave coatings that retained opacity after wetting, were ineffective. Thus, although it was possible to obtain good adhesion and wet rub

resistance, it was never achieved with a coating that exhibited good retention of opacity after processing.

Improvement of Opacity Retention - The opacity of the microcapsule coating depends on the loss of solvent from the capsules during drying of the coating and it was assumed that the aggregate of closely packed microspheres served as light scattering centers. Loss of opacity was attributed to the fact that capsules formed by interfacial polycondensation are generally porous and could fill with solution during processing, thus becoming transparent.

The fact that opacity depends on the loss of solvent can be readily confirmed from experimental observations. Transparent microcapsule coatings, if scratched, release solvent in the track of the scratch where capsules are broken; opaque coatings do not. It is possible to prevent cumene-containing microcapsules from becoming transparent either by drying the gelatin-containing coating thoroughly at room temperature before heating to 90°C (organic solvents can only migrate through gelatin if it is in a swollen state) or by coating the capsules in polyvinyl alcohol which forms a good vapor barrier. Transparent coatings of cumene microcapsules in gelatin can be rendered opaque if the coating is placed in a 90°C oven along with a container of water. Under these conditions the vapor pressure of water is high enough to swell the gelatin and allow the solvent to escape.

The reasons for the loss of opacity cannot be as readily pinpointed. Filling of the capsules with water or any other transparent liquid would indeed render the coating transparent. In preparing the coating, the cumene core of the capsules is lost before opacity is achieved. Why then, when the wet processed DTM is redried, does the water not escape from the capsules to return the coating to an opaque state? It is possible since there always is a vapor pressure of water in the atmosphere, that water, once inside the capsules would tend to remain unless subjected to temperatures above its boiling point. It is also possible that hydrogen bonding between water and groupings in the polymer wall could aid in retention of the water. However, there are other factors that may contribute to opacity loss.

In making the capsules there is initially only enough binder present to stabilize the microdroplets of organic solvent created by the ultrasonic dispersion technique. By the end of the preparation process the binder concentration is approximately 1.3% of the total weight. If the microcapsule suspension is allowed to stand without adding the additional binder required before coating, the cumene microcapsules will, in time, float to the top of the container as their density is less than that of water. The polyamide nature of the capsule wall makes it somewhat hydrophobic and probably not totally compatible with binders such as gelatin or polyvinyl alcohol. In the DTM coating there is an exceptionally high packing density of microcapsules. Assuming that all of the cumene initially used ends up inside spherical capsules 5  $\mu$ m in diameter, calculations indicate that each square foot of coating contains approximately 10 trillion microcapsules. Admittedly, there are losses along the way but even if these amounted to a factor of 1000 the number of capsules present is still very large. The same square foot of coating contains less than 200 mg of coating vehicle.

When the coating becomes saturated with water the vehicle swells and, if stress is applied by ribbed rollers or other contact surfaces, it is quite possible that displacement and even loss of some of the microcapsule content of the coating can occur. Lessening of the packing density of the capsules would, of course, reduce the opacity.

An additional possibility is related to the nature of the capsule wall. It is a polyamide that fits in the nylon category of polymers. In relation to other polymers, nylons are less resistant to attack by chemicals. In the course of processing them, it is quite probable that some capsules will be destroyed by chemical attack or at least damaged enough to lose their spherical shape and, thus, their capability to act as scattering centers. If all three of the conjectured mechanisms (plus others as yet not considered) can occur during a processing test, it is easy to see why the loss of opacity can be severe. However, the problem, regardless of its cause, is not an insurmountable one. Although none of the experimental coatings has survived a full processing cycle without some loss of opacity, some have retained more than enough to delineate scratches with good contrast.

Through most of the experimental program filling of the microcapsules with water was assumed to be the main loss mechanism. Accordingly, the formulation changes were designed to prevent this process from taking place. A series of cumene-soluble polymers such as polystyrene, polymethyl methacrylate, chlorosulfonated polyethylene, chlorinated rubber, ethyl cellulose and polyvinyl acetate were dissolved in the cumene prior to dissolving the terephthaloyl chloride. When the capsules were formed the cores contained polymer-saturated cumene. Since the cumene is presumably lost through the pores in the capsule wall, it was hoped that the polymer would deposit in these pores as the cumene volatilized and block them. The polymers tended to aid in preventing the loss of opacity when the DTM was processed but not all of them were effective. As an alternative, water repellents were dissolved in the cumene in an attempt to prepare capsules that would resist the intake of water because their pores would be waterproofed. This approach met with little success although, as discussed in the section on adhesion, one of the preparations did lead to an adherent DTM with good wet rub resistance. The mobility of the cumene in the liquid state was also lowered in some formulations by thickening it with thixotropes in an effort to keep it from leaching into the aqueous phase.

An approach intended to increase the compatibility between the capsules and the gelatin binder, the incorporation of hardening agents in the cumene phase during capsule making, was unsuccessful because of experimental difficulties. The intent of this variation was to cause localized hardening of gelatin around the capsules as the cumene diffused through the pores and contacted the gelatin-rich aqueous phase. Unfortunately, all of the available hardening agents were too water soluble and extracted from the cumene into the water during the emulsification step thus causing premature hardening of the binder. We were able to demonstrate a beneficial effect from this approach only in the case of cyanuric chloride which, although not generally classed as a gelatin hardener, appears to interact with gelatin in some way.

Opacity retention after wet processing was also improved by the presence of



polyvinyl alcohol, particularly the more fully hydrolyzed, hot water soluble grades. The latter were, however, good vapor barriers and the coated samples often did not reach full opacity for several days after coating. The changes in opacity brought about by solution treatment of various DTM formulations were evaluated by making reflectance measurements. Data obtained are summarized in Table 1. Since all measurements were made on hand coatings after hand processing, uniformity is somewhat variable. Therefore the reflectance densities are given as ranges rather than average values

Table 1  
Changes in Opacity of Wet DTM after Photographic Processing

Additive to Cumene Phase	Type	Binder*	Reflectance Density**	
			Original	Processed
Cab-o-sil	Thixotrope	1.3% Gelvatol 20-90 2.7% Gelatin	0.57-.62	0.68-.84
Cyanuric chloride	Cross-linker	1.3% Gelvatol 20-60 1.7% Gelatin	.32-.34	.42-.46
		1.3% Gelvatol 20-90 2.7% Gelatin	.23-.36	.45-.51
Chlorosulfonated polyethylene	Polymer	4% Gelatin	.22-.26	.34-.50
		1.3% Gelvatol 20-90 4.7% Gelatin	0.32	.70
		1.3% PVA, 98% hydrolyzed 2.7% Gelatin	.34-.37	.47-.54
		1.3% PVA, 100% hydrolyzed	.40-.51	.42-.58
		1.3% PVA, 100% hydrolyzed 4.7% Gelatin	.48-.54	.38-.56

\*Gelvatols are Monsanto grades of polyvinyl alcohol. PVA = polyvinyl alcohol.

\*\* Background reflectance density of matte black polyester 2.1 - 2.2

Unfortunately, the ability to retain opacity after processing did not go hand in hand with ability to resist wet rubbing. The addition of chlorosulfonated polyethylene to formulations also containing the waterproofing agent 3-heptafluoroisopropoxypropyltrichlorosilane did not prevent the latter compound from providing good adhesion and wet rub resistance but it also did not counteract the severe loss of opacity exhibited by the silane-containing DTM.

Control of Repellencies - To prepare quality coatings of wet DTM, it was also necessary to determine the cause or causes of the repellencies found in hand coatings. This problem had been solved for the SO-192 substrate by controlling the method of application of the formaldehyde undercoat so that all of the aqueous formaldehyde was absorbed by the processed film before the microcapsule coating was applied, and by increasing the viscosity of the microcapsule suspension to prevent it from flowing around the repellent areas. However, these techniques were not applicable to the subcoated dyed polyester because the relatively heavy coating of gelatin was not present on the substrate. Since the presence of free cumene in the aqueous phase cannot be avoided (even if all of the cumene ends up inside microcapsules, some of it will leach out through the pores in the capsule wall), the first experiments were designed to determine whether it was the source of the problem. To simulate the worst possible case, that where all of the cumene ends up in the water, the total amount of cumene used for a microcapsule preparation was emulsified into the total final volume of 5% gelatin. A coating of this emulsion on either subcoated or unsubcoated black polyester immediately broke up into isolated areas of coverage that dried with some degree of opacity to give a wallpaper pattern effect. Portions of the emulsion were taken and additives such as methanol and various types of wetting agents were incorporated. Each additive tended to reduce the diameter of the repellency spots but, with one exception, the coatings dried to an opaque condition. Only Aerosol OT was totally effective. Emulsion containing this anionic wetting agent gave a perfectly smooth, transparent coating with no trace of repellencies. The appearance of the coating could not be differentiated from that of a 5% gelatin layer that did not contain any cumene. Although several other anionic wetting agents were screened, none gave quite the same dramatic result.

The completeness of the control of repellencies by the Aerosol OT led us to the conclusion that no other factors had a major influence on the problem.

#### Alternative Approaches

With the solutions to the problems of wet rub resistance and retention of opacity seemingly antagonistic to each other, we examined some alternatives for preparing a wet DTM. Typewriter correction fluids contain a suspension of an inorganic pigment in a solvent containing a soluble binder. By choosing a suitable dilution it was possible to prepare a uniform coating of this type of material on the black matte polyester. The coating had a reflection density of 0.2 and was quite hard. It softened in processing solutions and could be scratched when wet. It was, however, water repellent in nature and did not swell and shrink the way film would under these circumstances. Its water repellency was responsible for its adhesion to the black

polyester because all attempts to incorporate some gelatin or to make the material more hydrophilic led to partial loss of the coating in solution.

Another line of investigation involved spray drying of the microcapsules in an attempt to remove all extraneous chemicals from the system. The spray dried capsules were difficult to handle because they became charged and tended to cling strongly to anything they contacted. Preparation of the amount of capsules needed for a coating would have required large scale industrial equipment. On top of that concurrent experimental work indicated that the capsule suspension could be allowed to settle, the aqueous phase could be removed, and the capsules could be washed free of amines. The harmful effects of any free cumene were counteracted by the addition of Aerosol OT to the suspension. Thus the main impurities could be controlled by simpler means.

The possibility that microcapsules with different properties might work better in this application than the polyamide-walled species was also tested. Capsules received from the Appleton Paper Division of NCR were representative of gelatin-walled materials prepared by NCR's coacervation technique. These capsules should have a lower porosity than capsules formed by interfacial polycondensation. However, the capsule suspension, as received, contained so much hardening agent that all attempts to add gelatin or polyvinyl alcohol as a coating vehicle resulted in a rapid insolubilization of the binder. The capsules could be washed free of hardener but they separated very slowly from the wash water and several washings were required. The washed capsules seemed to behave similarly to capsules prepared on this program.

#### COATING MACHINE SETUP AND MODIFICATION

Since the contract called for delivery of a sizeable quantity of wet DTM, it was necessary to have coating facilities available before the middle of the program. Accordingly, work had to be initiated immediately after purchase of the coater to install it in the Aerodyne laboratories and make the required modifications to adapt it for DTM coating. A schematic sketch of the basic arrangement of the coating machine is shown in Figure 1. To the basic coater a unit was added between the supply spool and the coating head to neutralize any static build-up on the polyester web and clean it. A hood with its associated venting system was placed over the coating head area to purge the solvent vapors emitted at this stage. The four enclosed areas within the machine had to be fitted with facilities for chill-setting gelatin coatings and for hot air drying of the set coatings. An air conditioning unit was installed and cold air ducts were connected to the first of the four chambers. Ceiling mounted hot air dryers were connected to the other three chambers. Baffling had to be installed between the first and second chambers to keep the cold air from lowering the temperature of the drying air. The machine and all of the auxiliary units had to be wired into the building electrical system, air lines had to be installed for the pneumatic clutches, and thermocouples had to be fabricated for monitoring temperatures at various locations in the chill and drying chambers.

The machine, as purchased, was set up to handle a 10 inch web of substrate.



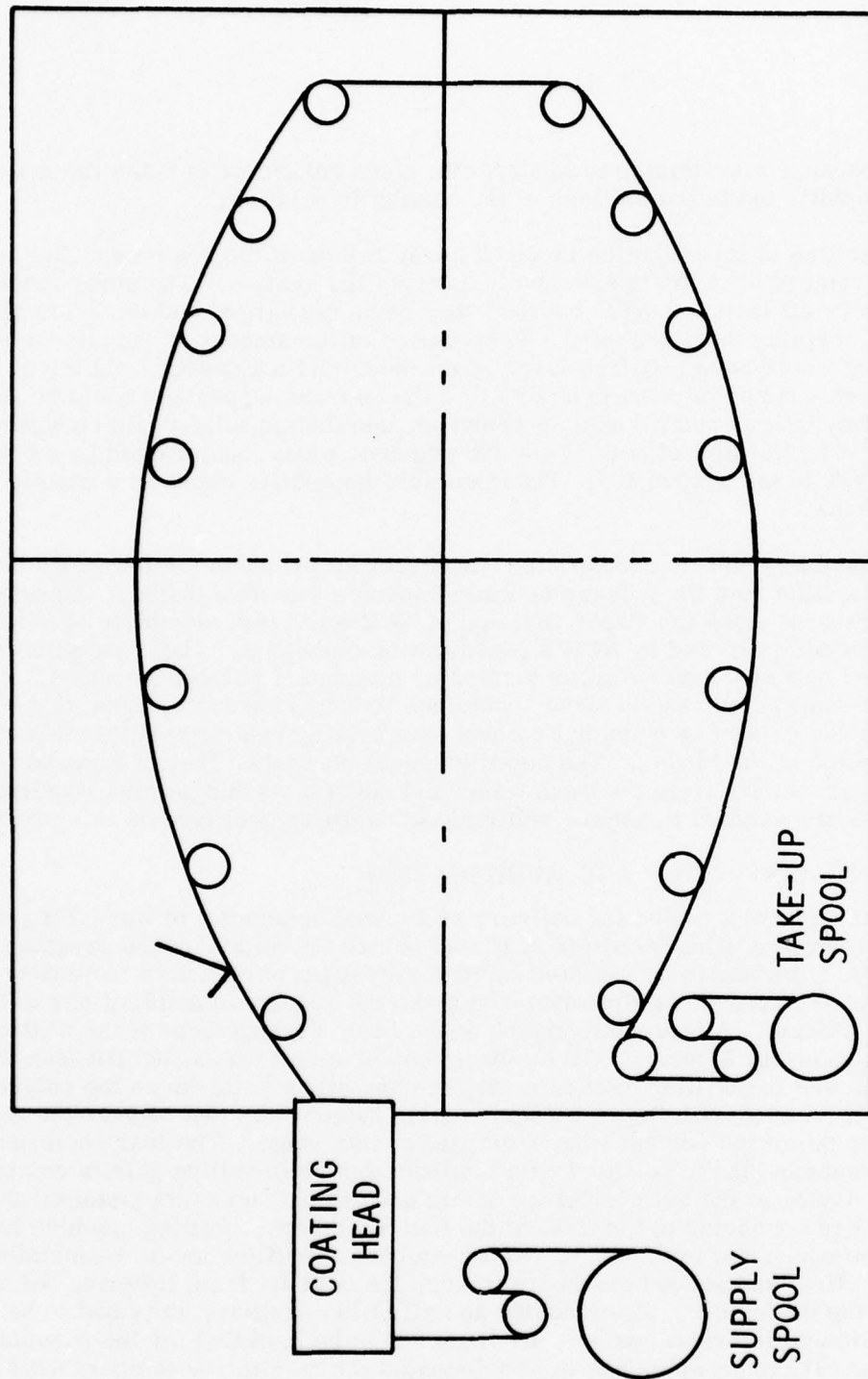


Figure 1. Schematic Arrangement of Coater Set Up for Use on This Program

Since the material to be delivered was slated to be 9-1/2 inches in width, this format did not allow much room for error. The full width of a web cannot be coated since solution will spill over the edges and collect on the transport rollers. Lateral movement of the coating suspension leads to a fall off in thickness and properties at the edge of the web. Since, in all probability we would need to coat both a subcoating layer from organic solvent and a microcapsule layer from aqueous solution, the edge problems would be compounded. Therefore, the machine was modified to handle an 11-1/2 inch web. The principal modifications required were the removal of internal magnetic door latches and installation of external latching mechanisms, replacement of the metal cover plates with transparent plastic ones, relocation of the brake, and the addition of x-y adjustments to rollers at both ends of the machine (to aid in tracking). Although several coating heads were furnished along with the machine, only the reverse roll head was utilized for setting up and testing. The only modifications required on this head were the grinding down of one roller that was undercut at both ends, and the addition of a longer drive belt since placement of the static eliminator/web cleaner necessitated moving the coating head further away from the enclosed portion of the machine. Cleaning and refurbishing of rollers, shafts, bearings, and slip clutches completed the revamping of the coater.

The rollers of the machine were aligned with the aid of a laser and an 11-1/2 inch web of black matte polyester was run through to check the tracking. A trial coating of typewriter correction fluid in trichloroethylene was made. A smooth coating was obtained and there was no wandering at the edge, which confirmed that the tracking was adequate.

### III EXPERIMENTAL

Since the primary purpose of the initial phase of the program was to find conditions of preparing wet DTM coatings of high quality, the first portion of the experimental section will detail the methods used to prepare the wet DTM coating delivered to the customer. Procedures used prior to this were ineffective and would only serve to confuse the issue. A summary of the various experiments mentioned will be included to illustrate the range of materials tried and the degree of success obtained. The experimental work conducted following the switch to the dyed polyester substrate will be reported in more detail. Since the problem of preparing a DTM with the desired properties was not completely solved, the experimental work should be detailed as a basis for selecting a path to follow should work of this nature be continued at some later date. Finally, the preparation and coating of the dry DTM will be described.

#### PREPARATION OF MICROCAPSULE COATING SOLUTION

A 9.6g portion of terephthaloyl chloride, 4g of triphenyl phosphite and 2.4g of Dow Corning 1108 fluid was weighed into a 250 ml ground glass stoppered erlenmeyer flask and covered with 116 ml of cumene. The flask was loosely stoppered and heated at 60°C until all the acid chloride dissolved. The cumene solution was then poured into a 400 ml beaker containing 200 ml of 2.5% Type 2403 gelatin (Peter

Cooper Corporation) solution. The beaker was placed on a magnetic stirring apparatus and a magnetic stirrer bar was placed in the solution. Vigorous stirring was initiated causing the upper organic layer to be drawn into a vortex and to mix with the aqueous phase. The probe from a Branson Sonifier Model J-17A was placed in the outer wall of the vortex and the power supply was operated at setting 2 for 30 seconds, then at setting 4 for an additional 30 seconds. Efficient emulsification occurred and examination of a sample of the emulsion under 400 X magnification indicated that the cumene droplet size was fairly uniform; the droplets were approximately  $2\mu\text{m}$  in diameter. While this emulsion was being stirred rapidly with the magnetic stirrer, a solution containing 6.4g of sodium carbonate, 3.2g of ethylenediamine and 2.4g of diethylenetriamine in 64 ml of water was instantaneously poured into the vortex. Microcapsules formed. Under the microscope there appeared to be a high degree of clumping of the capsules. However, reinsertion of the ultrasonic probe into the capsule suspension and operation of the power supply for 1 minute at a setting of 4 caused the clumps to break apart into individual capsules.

#### COATING OF WET DTM

Into a 250 ml graduated cylinder were poured 50 ml of 37% formaldehyde solution and sufficient methanol to bring the total volume to 200 ml. The solution was transferred to a 400 ml beaker which was placed under the feed line of coating station #1. The coating head at this station was fitted with a 5-3/4 inch wide piece of felt filling a 1/32" opening. The head was adjusted so that the felt just made contact with the web of 7 inch wide film and the solution was fed at such a rate that the methanol was completely evaporated before the film reached the second coating station.

The microcapsule suspension was filtered through a 50 micron viscose filter cone to remove any large particles that might tend to plug the coating head and 368g of material was collected in a 600 ml beaker. To this was added 160 ml of 15% Type 2403 gelatin solution. The beaker was heated in a water bath at 60°C and stirred (magnetic stirrer) for 15 minutes to ensure homogeneity. It was then placed under the feed line of coating station #2. Slow stirring was continued with the magnetic stirrer all during the coating. The coating head was fitted with a 5 mil shim and was kept warm (50°C) during the entire coating cycle. As only 165 feet of substrate remained on the roll of film being coated, the coating had to be terminated before all of the microcapsule suspension was used. The residual suspension weighed 95g. On this basis, the amount of suspension prepared would have been capable of coating 200 feet of substrate.

The initial portion of the coating, where conditions were being varied to establish an optimum, was cut from the roll. The remaining 125 feet of 7 inch wide DTM was slit to 6.6 inches. This was delivered to the customer as an approval sample.



## OVERCOATING OF DRY DTM

A batch of tetrachloroethylene-filled microcapsules was prepared by dissolving 10g of terephthaloyl chloride in 100 ml of tetrachloroethylene at elevated temperature (60°C); pouring the solution into a beaker containing 40g of 15% gelatin solution, 40g of 10% Gelvatol 20-60 (polyvinyl alcohol) solution, 8 ml of 5% saponin solution, and enough water to make a total weight of 400g; stirring with a magnetic stirrer to create a vortex; emulsifying with the Branson probe placed in the wall of the vortex 15 seconds at power supply setting 2 and 45 seconds at setting 4; and adding a solution of 6.4g sodium carbonate, 3.2g ethylenediamine and 2.4g diethylenetriamine in 64 ml of water. The suspension of microcapsules was agitated for 1 minute with the ultrasonic probe (power supply setting 3.5) to break up aggregates and filtered through the 50 micron viscose filter cone. To the 605g of filtrate was added 300g of 15% gelatin solution to adjust the final binder concentration to 6.6%. This suspension was coated on the multi-head coater with a 3 mil shim in the coating head. Approximately 200 feet of usable area was obtained.

Since the polyamide capsule walls appear to be attacked by alcohols, water insoluble polymers that could be dissolved in solvents other than alcohol were used in the overcoating experiments. Commercial flexible collodion solution, which comes in a mixture of ether and alcohol, was diluted with toluene. As the toluene was added precipitation occurred but, on stirring, the precipitate redissolved. Saran F 120 resin was dissolved in a mixture of methyl ethyl ketone and acetone. Piccolastic (polystyrene) resin was dissolved in toluene. A Minwax polyurethane varnish was used directly from the can. Carboset 525 resin was also dissolved in toluene. Each of these solutions was coated (multi-head coater) over a section of the dry DTM prepared above. The flexible collodion, Saran and polyurethane varnish coatings appeared to be most resistant to the access of water. The Carboset resin retained some tackiness and caused the overcoated DTM to stick to itself on the take-up roll.

All of the overcoated samples of dry DTM showed similar properties. They tended to opaque on storage at a slower rate than the unovercoated dry DTM. They were less sensitive, not responding readily to 1 or 2g weights on the stylus of the scratch tester. There was a delay of several seconds before the white mark appeared at the location of a scratch, as the solvent released on capsule breakage could not escape as rapidly as from the surface of the unprotected DTM.

## ATTEMPTED PREPARATION OF MICROCAPSULES CONTAINING LOW BOILING SOLVENTS

Low boiling solvents screened included tetramethylsilane (24°C), ethyl bromide (38°C), methylene chloride (40°C), and Freon TF (47°C). The standard procedure was to try to dissolve from 0.6 to 1.2g of terephthaloyl chloride in the solvent, disperse the resulting solution in 50 ml of 2.5% aqueous gelatin with the ultrasonic probe, and form microcapsules by adding 8 ml of water containing 0.8g sodium carbonate, 0.4g ethylenediamine and 0.3g diethylenetriamine to the dispersion. It was necessary to cool the solutions in ice to prevent boiling of the solvents during these operations.

#### Tetramethylsilane

Tetramethylsilane was refluxed with 1g of terephthaloyl chloride but a negligible amount of the chloride dissolved. Microcapsules were formed but they were few in number. When the suspension was warmed and stirred to drive off the unencapsulated solvent vigorous foaming ensued and it was difficult to keep the reaction within the confines of the container.

#### Ethyl Bromide

When 15 ml of ethyl bromide failed to dissolve 0.6g of terephthaloyl chloride, 5 ml of cumene was added as a cosolvent. Microcapsules formed but they appeared to be too porous to confine the ethyl bromide. Normally a droplet of capsule suspension is diluted with water and examined under the microscope to determine whether capsules did indeed form and to estimate the diameter of the capsules. These capsules float past the field of view at a certain rate. The ethyl bromide containing capsules passed the field of view at a much faster rate and appeared to be "jet propelled". In time, the spherical capsules gave way to a suspension of irregularly shaped particles. The suspension was hand coated on processed SO-192 and formed a smooth coating which was transparent and marked with poor contrast.

#### Methylene Chloride

Approximately 20 ml of methylene chloride was required to dissolve 1.2g of terephthaloyl chloride. When the preparation stages leading to microcapsule formation were completed, the sample examined under the microscope was found to contain relatively few capsules and many particles of irregular shape.

#### Freon TF

When 15 ml of boiling Freon TF failed to dissolve 1.2g of terephthaloyl chloride, 6 ml of tetrachlorethylene was added to complete the solution. Good capsule formation occurred but hand coatings of the suspension were transparent and behaved like a dry DTM.

#### ALTERNATE ATTEMPT TO REMOVE FREE SOLVENT

Since the microcapsules are prepared as a suspension in gelatin, we attempted to eliminate free solvent by techniques used for removing impurities from photographic emulsions. A cumene microcapsule suspension was prepared in the usual manner and 25 ml of the suspension was mixed with 100 ml of methanol. The gelatin precipitated along with the capsules. The methanol supernatant was decanted and attempts were made to wash the precipitated gelatin. Water chilled close to the freezing point seemed to peptize the solids so washing was accomplished with several fresh portions of methanol. The residual solids were mixed with enough 5% gelatin solution to bring the total volume to 35 ml. However, the capsules could not be resuspended even if the mixture was warmed and agitated with the ultrasonic probe.

Possibly the pressure exerted by the gelatin on coagulation destroyed some of the capsules and the solvent action of the methanol on the capsule wall material was too extensive to allow the capsules to survive this procedure.

#### ATTEMPTED IN-SITU MICROCAPSULE FORMATION

Since the suspension of droplets of cumene (containing dissolved terephthaloyl chloride) in aqueous gelatin is stable for a long period of time, an attempt was made to form the microcapsules directly on the substrate. The aqueous solution containing sodium carbonate and the polyamines was imbibed into pieces of processed SO-192. Hand coatings of the cumene-in-gelatin suspension were made using Meyer rods. Capsule formation was observed but the distribution over the film surface was very uneven. When the film was thoroughly dry, scratching with a sharp object caused solvent to be released. This confirmed the presence of capsules. The capsules formed in-situ still tended to wash from the film if it was placed in water. However, overcoating with a 10% aqueous formaldehyde solution improved the adhesion of the capsules.

#### ALTERNATIVE SUBSTRATE STUDIES

Three samples of dyed polyester were obtained from Martin Processing, a glossy-surfaced black, a matte-surfaced black and a subcoated, glossy-surfaced red. The subcoated material was prepared by dyeing an ICI product called Melinex 505 so samples of undyed Melinex 505 were obtained from ICI for comparison. (The subcoating is lacquer compatible and not meant for aqueous formulations). On hand in these laboratories was a roll of Gafstar, a commercially subcoated polyethylene terephthalate. The two undyed substrates were screened in the event that, if their subcoatings held the DTM layer well, they might be furnished with a dye layer on the back side to provide the desired black background.

The screening procedure consisted of preparing a solution of formaldehyde by diluting 1 ml of 37% aqueous formaldehyde to 10 ml with methanol, placing a pool of this solution at the top of the substrate and drawing a thin layer (with a #10 Meyer rod) across the length of the substrate. The methanol was allowed to evaporate, then a pool of microcapsule suspension was placed at the top of the substrate and a coating was drawn with a #25 Meyer rod. The coated DTM was dried in an oven held at 90°C, then allowed to stand overnight in air. Adhesion of the DTM coating was determined by 2 separate subjective tests. A strip cut from the coating was soaked for 7 min. in Kodak D-19 developer, rinsed in water, soaked 7 min. in Kodak Rapid Fix, then rinsed in water again. While still wet, it was marked with a plastic straw and another area was brushed lightly with a finger. If light brushing failed to remove any of the coating, the wet area was rubbed with a thumb to see whether the coating would be removed or displaced. As the hardener in the fixer toughened the DTM layer considerably, its resistance to plain water was determined on another portion of the coating. The full force of a sink spray unit, adjusted to give water at a temperature approximating that of the room, was directed onto the coating. If the coating was not washed from the substrate, it was subjected to light rubbing with the finger and,



resisting that, to more intense rubbing with a thumb.

With the exception of the red dyed Melinex 505, none of the substrates held the coatings well enough to pass these tests. The dyed Melinex had not wet smoothly and the coating came off in some areas but was held tightly enough in others to resist scrubbing with a brush. Unfortunately, Martin Processing had run into severe blocking problems when dyeing the Melinex 505 and they discontinued this product prior to the time we were ready to place an order. The dyeing, which is done at elevated temperature from organic solvent, obviously affected the properties of the subcoating because the undyed Melinex 505 did not hold the DTM layer well enough to resist even light rubbing.

#### Subcoatings for Glossy and Matte Black Polyester

Styrene/Maleic Anhydride (S/MA) - The S/MA polymer was a Scientific Polymer Products, Inc. item of 50,000 molecular weight. It dissolved slowly in acetone (with stirring) and was used as a 5% solution. A pool of solution was spread over the substrate with a #10 Meyer rod. The acetone evaporated rapidly and the coating was dried in an oven at 90°C. After drying, the coating could not be removed by putting down a piece of Scotch tape and pulling it sharply from the surface. The coating did not wet well with water. However, dipping it in dilute sodium carbonate solution hydrolyzed the anhydride groups and the coating then wet evenly. The hydrolysis affected the bond to the substrate since the wettable subcoating could be pulled from the base by Scotch tape.

Many variations on this subcoating were tested for improved bonding to the substrate. The most successful were an S/MA coating containing cyanuric chloride and an S/MA coating partially aminolyzed with a high molecular weight amine. For the former, 1 ml of a saturated solution of cyanuric chloride in acetone was added to 5 ml of 5% S/MA solution. For the latter, a 7.5% solution of Hercules Amine D in acetone was added dropwise, with stirring to an equal volume of 10% S/MA in acetone. The S/MA-cyanuric chloride subcoating bonded gelatin tightly. A 5% gelatin coating applied with a #15 Meyer rod on either subcoated glossy or matte black base could be carried through a full development cycle and, while still wet, could be rubbed vigorously with maximum thumb pressure without loss or displacement of the gelatin. A primitive photographic emulsion coated on the same subbing could be treated similarly and the processed image was not displaced or otherwise affected by vigorous thumb pressure.

Polymers with low or no water solubility that were mixed with the S/MA polymer to keep it from loosening from the base after hydrolysis included Saran F120, cellulose acetate, polyvinyl acetate, Piccolastic D-100 (polystyrene), Parlodion (nitrocellulose), Polyrad 515 (Amine D-ethylene oxide condensation product) and Bakelite VMCA (terpolymer of vinyl chloride, vinyl acetate, and maleic acid). Additives to S/MA that might influence bonding between the subcoating and microcapsule coating included silicon tetrachloride (hydrolyzes to silicic acid), tetraisopropyl orthotitanate (hydrolyzes to titanium dioxide), a commercial packaged epoxy, Union Carbide Silane Adhesion Promoters A1120 and A186, Sumstar (a dialdehyde starch), 2,5-dimethoxy-2,5-dihydrofuran and 2,5-dimethoxytetrahydrofuran.

Gelatin - Prepared acid gelatin solutions in solvents capable of attacking polyester as follows:

A. A 0.35g portion of gelatin was mixed with 6g of trichloroacetic acid (solid) and 0.7g of water was added to dissolve the acid. After the gelatin had soaked overnight, warming and stirring with a glass rod gave a homogeneous solution. When this was coated with a #10 Meyer rod on dyed polyester, partially dried in an air current, washed free of acid by immersing several times in fresh changes of water, and dried at 90°C, it formed a subbing layer with a whitish cast. The substrate remained perfectly flat and the coating passed the Scotch tape test. Microcapsule coatings applied over this subbing layer were not held well. The use of an intermediate formaldehyde coating improved the bond but the resultant DTM coating tended to lose some surface material when immersed in water. The best result obtained with material subcoated in this manner was when a 5% solution of S/MA in acetone was coated over it before applying the formaldehyde and microcapsule coatings. Application of the S/MA caused release of black dye from the substrate surface. The doubly subcoated polyester was dried at 90°C and aged in air prior to use. The DTM formed on this substrate had poor opacity but good wet rub resistance whether just wet with water or wet as a result of processing. Wetting and subsequent drying of the DTM actually increased its opacity.

B. A 2.75g portion of gelatin (Type 2403, Peter Cooper Corp.) was covered with 22.25g of dichloroacetic acid. After soaking overnight the gelatin had swelled enough that, on warming and stirring of the mixture, a homogeneous solution was obtained. When this was coated with a #10 Meyer rod on dyed polyester and coated substrate was dried at 90°C, severe curling of the substrate was noted. Modification of the procedure by washing the excess acid out of the gelatin subcoating prior to drying at 90°C did not remedy the curl problem.

C. Covered 0.5g gelatin with 5.8g m-cresol. Over a period of days the gelatin seemed to absorb the cresol and form a homogeneous cake on the bottom of the container. Broke up the cake with a glass rod and mixed with a supernatant cresol until a homogeneous mixture was obtained. Drops of this mixture were added to various solvents. Only methylene chloride failed to precipitate the gelatin. Coatings from methylene chloride on black polyester were very thin and had to be washed to remove the cresol, which thinned the coating even more. Droplets of a solution containing 1g gelatin in 3.68g m-cresol (21.4% compared to 7.9% for the initial solution) also could be dispersed in methylene chloride and coated. With the higher gelatin to cresol ratio it was not necessary to wash the subcoated base to remove excess cresol. Microcapsule layers coated on this subbing held well but lost their opacity in solution. Formaldehyde undercoating caused the DTM to have a distinct pink color. When processed DTM coatings on this gelatin subcoating dried thoroughly some of the coating lifted from the base. Apparently, the gelatin had not formed a solid bond to the substrate.

In addition, gelatin was applied directly to the substrate from both water-in-oil and oil-in-water type emulsions. Initially 12g of methylene chloride, which was known

to attack the dyed polyester surface, was emulsified into 25g of 1.25% gelatin solution in the manner used for emulsifying the cumene solution of terephthaloyl chloride (described later in the experimental section). Once emulsified the droplets of organic phase ( $\sim 5\mu\text{m}$  in size) are stabilized by the gelatin and the emulsion does not separate for several hours. However, when this emulsion was coated on the dyed polyester substrates, it did not wet well and the gelatin coating deposited was not tightly bound. To produce an emulsion with a methylene chloride outer phase 2.75g of Morpel X-914 (a petroleum sulfonate) was dissolved in 24.4g methylene chloride. While stirring, a warm 5% gelatin solution was added to this solution from a medicine dropper until the mixture clouded ( $\sim 7\text{ml}$ ). The emulsion was agitated by means of an ultrasonic probe to reduce the droplet size of the emulsified gelatin solution. Then it was coated on the dyed polyester with a #10 Meyer rod. A smooth coating that passed the Scotch tape test resulted. Microcapsule suspensions coated on this subbing were repelled. Petroleum sulfonates are such efficient emulsifiers that they carry approximately 40% of oil with them when they are extracted from acid treated oil. Thus there was approximately 3 times as much oil as gelatin present in the emulsion and this probably contributed to the incompatibility. Attempts to wash out the oil also removed the gelatin since both oil and emulsifier were present. The small areas of the subbing that did not repel the microcapsule suspension were resistant to wash-off even on soaking in water for 30 minutes.

A number of other emulsifiers that were more oil than water soluble were screened to see whether they could be used in place of the Morpel. These included Polyrad 515 (Hercules), Surfynol 440 (Air Products), Alkaterge T (IMC) and Witcamide 511 (Witco). However, none formed as stable an emulsion as the Morpel.

Experiments on controlling repellencies had indicated that Aerosol-OT (American Cyanamide) or its active ingredient sodium dioctyl sulfosuccinate was a unique emulsifier for dispersing both hydrocarbons and chlorinated hydrocarbons in gelatin solutions. Some of these emulsions, when coated on the dyed polyester, produced coatings that passed the Scotch tape test. A typical procedure is described here. Poured 15ml tetrachloroethylene into 25 ml of 5% gelatin solution, stirred the mixture with a magnetic stirrer, and subjected it to ultrasonic treatment for one minute. An emulsion was obtained that remained stable overnite. When coated on the black polyester, the emulsion was repelled strongly. When 0.5g of Aerosol OT (75% solution) was added and the emulsion was warmed and stirred with a glass rod until homogeneous, a smooth coating could be obtained from the end product. (Ultrasonic agitation caused foaming when the Aerosol OT was present). This coating was not lifted from the substrate by Scotch tape. It wet evenly and, after drying, still was not removable by Scotch tape.

Similar results were obtained with emulsified 1,2-dichloroethane, methylene chloride and 1,1,2-trichloroethane.

Photozid - Photozid (Upjohn) is a photoactive (sulfonylazide) polymer. Nitrene free radicals formed from it as a result of exposure to ultraviolet radiation are reported to pair up with electrons on the substrate surface. The photolyzed product then becomes an integral part of the surface and should not be removable



by any ordinary means. The backbone of the polymer contains pendant carboxyl groups which should be compatible with gelatin. The Photozid can also be broken down thermally at temperatures above 100°C to generate the same nitrene radical.

An 8% solution of Photozid in acetone was prepared by stirring 2g of Photozid with 25 ml of acetone until all was dissolved. Portions of this solution were coated on the dyed black polyester. The solvent evaporated rapidly leaving a smooth, transparent coating. One piece of substrate served as a control, another was heated at 110°C and a third was irradiated with an ultraviolet lamp that emitted primarily 254 nm radiation. All three were held tightly enough to the substrate to pass the Scotch tape test. The heated sample was somewhat deformed by the heat treatment. None of the samples wet evenly with water. Since unionized carboxyl groups are not hydrophilic, the samples were dipped in a dilute sodium carbonate solution to promote ionization. After this treatment, water filmed smoothly over the surface of the films. Testing indicated that the undecomposed Photozid made a better bond to the base than either the photolyzed or thermally decomposed polymer. Photozid coatings had two serious drawbacks. At high developer pH they were solubilized to a degree and the bond to the base was weakened. Also, for some reason, microcapsule coatings on this subbing tended to lose their opacity totally on processing.

Carboset XL-19 - A milky aqueous solution of a carboxylated resin containing 40% solids content (solubilized as the ammonium salt), Carboset XL-19 (B. F. Goodrich) could be coated directly onto the dyed black polyester to form a smooth, glossy, transparent subbing layer. The layer, dried at 90°C, adhered strongly to the substrate but was not particularly hydrophilic. Microcapsule coatings on this subbing showed excessive repellencies. In the drying process the Carboset coating insolubilizes by loss of ammonia. Therefore, an attempt was made to coat the microcapsule layer over the Carboset before the subbing layer was dry. The two materials were incompatible. The components of the microcapsule suspension were tested for reaction with Carboset. The two polyamines, diethylenetriamine and ethylenediamine, used in excess in the capsule forming step, both caused immediate precipitation of the Carboset from solution. Gelatin appeared to be compatible with Carboset but, when samples where gelatin was coated with Carboset were cycled through processing solutions, evidence of incompatibility was noted; the gelatin layers on the processed strip tended to crack on drying.

The diamines were cleaned from a tetrachloroethylene-containing microcapsule preparation by allowing the capsules to settle, drawing off the supernatant liquid, resuspending the capsules in fresh water, allowing them to settle, and repeating the process until a drop of the supernatant liquid did not cause precipitation when added to a drop of Carboset XL-19. A 1.6g portion of settled, washed capsules was mixed with 0.9g Carboset, coated with a #15 Meyer rod on the glossy black polyester, and dried at 90°C. The coating adhered well to the base but dried transparent. When cycled through the processing solutions it gained some opacity in the first wash and showed scratch marks but, on drying, the opacity was lost. If the settled washed capsules were mixed with an equal weight of 20% gelatin solution and coated on the Carboset subbing, the coating cracked on drying.

Miscellaneous - Several other polymers were screened as possible subcoating materials. Chlorosulfonated polyethylene applied from toluene, acetone or methylene chloride formed an adherent but water repellent coating. Additives were incorporated to try to make this subbing layer hydrophilic. Cab-o-sil (Cabot), a silica aerogel, acted as a thickener for toluene and methylene chloride solutions of the polymer. Coatings of chlorosulfonated polyethylene from these solvents dried to give a rough grainy surface which passed the Scotch tape test and wet well with water. However, when gelatin was coated over the subcoating and dried, Scotch tape pulled both layers from the base. Silicone adhesion promoter A-1120 also imparted hydrophilic character to the polymer subbing. Microcapsule coatings on this subbing had poor wet rub resistance. Two attempts were made to incorporate gelatin into the solutions of chlorosulfonated polyethylene. A solution of the polymer in methylene chloride tolerated 1 drop of 7.9% gelatin in cresol. A coating of this mixture dried to a dull finish and passed the Scotch tape test. It wet evenly and drained slowly. However, as subsequent tests confirmed, the dissolving of gelatin in m-cresol affects the properties of the gelatin and prevents it from bonding to fresh, untreated gelatin. A mixture of chlorosulfonated polyethylene and polyvinyl formal coated on dyed black polyester from toluene/methylene chloride could be overcoated with a solution of gelatin in acetic acid that contained some dissolved Pyroxylin. This doubly subcoated substrate coated with a microcapsule suspension showed minimal repellencies but had poor wet rub resistance.

Polyvinyl alcohol and a polyvinyl alcohol containing terpolymer were also screened. The terpolymer was a vinyl chloride/vinyl acetate/vinyl alcohol polymer. It was soluble in acetone and methylene chloride but exhibited variable behavior when coated on the dyed black polyester. Sometimes the bond formed resisted pulling with Scotch tape, other times it did not, and still other times it pulled up in some areas but not in others. It was not particularly hydrophilic, but when Aerosol OT was present in the microcapsule suspension, no gross repellencies were obtained. Gelvatol 20-60 (Monsanto) was dissolved in diethylenetriamine. Dilutions with solvents such as acetone or methylene chloride caused precipitation so the subbing was coated directly from the triamine. The coated polyester was placed in an oven held at 90°C for two minutes, then was removed and immersed in cold water to wash out as much amine as possible. The washed subbed base was dried at 90°C. It wet very evenly. These subcoatings did not bond well to the microcapsule layer even when crosslinkers such as formaldehyde or 2,5-dimethoxytetrahydrofuran were included in the subbing formulation.

Other materials tried cursorily were a vinyl pyrrolidone/ethyl acrylate copolymer, Carbopol 934, Rhoplex (Rohm and Hass), a methyl vinyl ether/maleic acid copolymer and various nitrocellulose compositions with and without added gelatin. Bonding to the base was poor for all of these materials. Collodion if added to methylene chloride formed a gel which, when coated on the dyed black polyester, adhered well. However, gelatin would not stick to this subcoating.

More drastic modification of the polyester surface was attempted to see whether improved bonding would result. Sandblasting, treating with a Tesla coil and oxidation with alkaline potassium permanganate solution all failed to lead to improved adhesion.

## VARIATIONS ON MICROCAPSULE PREPARATIONS

The general procedure for preparing the microcapsule suspensions to be used in forming the DTM coating has been described earlier in this experimental section. As variations were made in an attempt to improve adhesion to the subcoating and to prevent loss of opacity after wet processing, the preparative technique was modified and improved. The ratios of the reactants remained the same but some minor changes were found beneficial. Emulsification of the cumene solution of terephthaloyl chloride into the 2.5% aqueous gelatin produced a very thick viscous mass and, although this thinned considerably when the amine-carbonate solution was added, efficient mixing was often impossible at this critical capsule forming stage. Two ways were found to keep the emulsion more fluid. Replacement of the gelatin by an equivalent concentration of polyvinyl alcohol not only prevented the increase in viscosity but also led to a more cohesive DTM layer. Gelatin could be retained as the protective colloid if 0.8% of sodium dioctyl sulfosuccinate was dissolved in the cumene solution along with the other ingredients. Studies on the interfacial polycondensation reaction indicate that better polymer formation occurs if an excess of the polyamine solution is always maintained. Therefore, after forming the emulsified cumene in gelatin, the emulsion was poured slowly into the stirred amine-carbonate solution. This change in procedure produced microcapsule suspensions with considerably less clumping and led to faster filtration.

The various microcapsule preparations were tested by the following procedure:

1. The capsule suspension was subjected to ultrasonic agitation for 1 minute on setting 3 to break up all clumps, then it was filtered through a 50 $\mu$ m cloth filter.
2. Portions of the filtrate, which contained approximately 1.3% binder (polyvinyl alcohol or gelatin), were weighed into separate containers and sufficient 15% gelatin solution was added to bring the binder content to 3, 4 and 5%.
3. The filtrate and the samples with higher binder contents were coated on S/MA subcoated black polyester, with or without added hardeners, chilled until the coating had set, then dried in an oven to a final temperature of 90°C. The coatings were allowed to stand overnight before they were evaluated.
4. A portion of each coating was immersed for 7 min. in D-19, rinsed in water, immersed 7 min. in Kodak Rapid Fix and rinsed again. The damp strip was marked with a plastic straw. Another area was rubbed lightly with the little finger. If no material was removed, the area was rubbed more vigorously with thumb pressure.
5. A portion of each coating was soaked in water for 2 min. then tested by rubbing as described above.



6. The opacity and contrast of the mark on the processed portions of the coatings was visually evaluated on both the wet strips and the strips after they had dried.

#### Lowering of Capsule Wall Porosity

Polymer Incorporation - Saturated solutions of polymers found to be soluble in cumene were prepared by covering 1 to 2g of polymer with 25 ml of cumene, stirring with a magnetic stirrer for one hour at room temperature, then for one hour at 60°C. The solutions were then allowed to stand at room temperature overnight. The polymer saturated cumene was substituted gram for gram for cumene in the microcapsule preparations. The triphenyl phosphite and Dow-Corning 1108 fluid were not included in the polymer containing formulations to minimize possible incompatibilities. Polymers soluble in cumene included chlorosulfonated polyethylene, polystyrene, polymethyl methacrylate. Hycar 1002 latex (Goodrich), polyvinyl acetate, Elvaloy 741 and 742 (DuPont) and ethyl cellulose. Ethyl cellulose behaved somewhat like a thixotrope for cumene. When the saturated solution had cooled to room temperature, it gelled but the gel could be partially restored to a fluid state by shaking the container. Most of the polymers had a beneficial effect on the solubility of terephthaloyl chloride in cumene. Less heating was required to dissolve the acid chloride and the solution formed could be cooled to a lower temperature before solid began to separate. The results of the evaluation of DTM coatings made from the polymer containing microcapsule preparations were as follows:

1. Chlorosulfonated polyethylene - Fully processed coating at 5% binder concentration kept the opacity well and had wet rub resistance. Strip wet with just water had poor wet rub resistance, even though chrome alum was added to the microcapsule suspension just prior to coating. Tried increasing binder content to 6 and 8%. Retention of opacity was still good but wet rub resistance did not improve.
2. Polymethyl methacrylate - Fully processed coating lost some opacity but retained enough for a mark to show. Wet rub resistance was poor but improved as the binder concentration was increased.
3. Polystyrene - Fully processed strip exhibited fair retention of opacity at 5% binder level but had poor wet rub resistance.
4. Hycar 1002 latex - Fully processed strip retained its opacity well but had poor wet rub resistance.
5. Polyvinyl acetate - Fully processed strip lost much of its opacity but had fair wet rub resistance.
6. Elvaloy 741 and 742 - Fully processed strips showed loss of opacity and poor wet rub resistance.

7. Ethyl cellulose - Because of the aforementioned tendency of this polymer to behave as a thixotrope for cumene, the microcapsule preparation turned out somewhat different than all the others. Microscopic observation indicated the presence of some very large capsules that appeared to contain many smaller capsules in their core. As a result the coatings obtained were grainy and had poor wet rub resistance. Retention of opacity on processing was poor but improved as binder concentration was increased.

Thixotropes - Four thixotropes were evaluated for restricting the mobility of cumene from the microcapsules. They were Bentone 27 and Bentone 34 (NL Industries), Cab-o-sil and Silanox (Cabot). An additional thixotrope, that thickened water, was also screened. Both Bentones were dispersed in cumene using a Brinkmann Polytron followed by ultrasonic agitation. A 1% concentration was used. While some thixotropy developed, the Bentones showed some tendency to settle out on long standing.

The proportion of triphenyl phosphite normally included in a microcapsule preparation was added and the Bentones were redispersed. (Polar molecules often help to develop thixotropy). The Bentone 34, which seemed to be a better thixotrope for cumene than the Bentone 27, gave a DTM that retained opacity after processing but had poor wet rub resistance. The Bentone 27 preparation gave a DTM that was poor on both counts. Cab-o-sil (a hydrophilic silica) dispersed in cumene with minimal stirring (glass rod) with immediate development of thixotropy. Silanox (a hydrophobic silica) had to be used at a 4.8% level to develop thixotropy and ultrasonic agitation was required for complete dispersion. The Cab-o-sil containing DTM did not lose opacity on processing but was not highly opaque to begin with and had poor wet rub resistance. The Silanox containing DTM lost opacity on processing but, if the binder level was raised to 6%, had good wet rub resistance.

The thixotrope for water, a product of the Baker Castor Oil Co. (now part of NL Industries) labeled EA-1030, was added to water at the 1% concentration level and dispersed using the Brinkmann Polytron followed by ultrasonic agitation. Since the thixotrope is alkaline, the pH of the water was adjusted to neutral with 1N hydrochloric acid. The thixotropic water was used to replace the 2.5% gelatin or polyvinyl alcohol solution into which the cumene solution of terephthaloyl chloride is emulsified. The emulsion was very thick and difficult to handle but the microcapsules formed had a normal appearance. When coated without added binder, this formulation produced a DTM that totally retained its opacity after processing. As gelatin was added to build up the binder concentration, the DTM layers coated tended to lose opacity on processing. All coatings were lacking in wet rub resistance but those with no added binder or with the lower binder concentrations, also had poor dry rub characteristics. The coatings were rough-surfaced and movement of a finger along the dry DTM coating tore the coating.

In another preparation, the cumene solution of terephthaloyl chloride was emulsified into 2.5% aqueous polyvinyl alcohol and the emulsion was added to an amine-carbonate solution that had been made up with thixotropic water. In this

case, opacity was lost by all coatings but the loss was less at the higher binder concentration.

Cross Linkers - Most of the normal gelatin cross linkers that were soluble in cumene were extracted into the aqueous phase on emulsification and caused premature hardening of the binder. Only cyanuric chloride, which appeared to increase the strength of bonding to gelatin when incorporated into the S/MA subcoating, was retained by the cumene. To 14 ml of cumene were added 0.7g cyanuric chloride and 1.2g terephthaloyl chloride and the mixture was heated to dissolve the solids. The cumene solution was then emulsified into 25 ml of 2.5% Gelvatol 20-60 in the usual manner and the emulsion was added to a stirred solution of 8 ml of water containing 0.8g sodium carbonate, 0.4g ethylenediamine and 0.3g diethylenetriamine. The microcapsule suspension was treated as described previously and the coatings made from it were found to retain their opacity fairly well after processing. However, the wet rub resistance of the coating was poor.

#### Binder Variation

Polyvinyl alcohol is available in several degrees of hydrolysis and in a number of molecular weights. Since the presence of polyvinyl alcohol seemed to lead to improved integral film strength in DTM coatings, we made a series of microcapsule preparations in which the only variation was the type of polyvinyl alcohol used. In all cases the cumene used was saturated with chlorosulfonated polyethylene. The properties of the polyvinyl alcohols are summarized in Table 2.

Table 2  
Properties of Polyvinyl Alcohols

Type	Source	Hydrolysis	Molecular Weight
Gelvatol 40-20	Monsanto	73-77	3,000
Gelvatol 20-60	Monsanto	86-89	96,000
Gelvatol 20-90	Monsanto	86-89	125,000
Polyvinyl alcohol	Aldrich	98	126,000
Polyvinyl alcohol	Aldrich	100	115,000

All of the polyvinyl alcohols were used at the 2.5% concentration level with the exception of the Gelvatol 40-20. Because of its very low molecular weight, it was used at the 10% level where its viscosity in solution approximated that of a 2.5% Gelvatol 20-60 solution. The two highly hydrolyzed grades are not cold water



soluble. The 100% hydrolyzed grade did not appear to be as good a protective colloid for stabilizing the cumene droplets since, after the usual emulsification procedure, a slick of cumene could be seen floating on the surface of the aqueous phase.

The behavior of DTM coatings prepared from these microcapsule preparations was somewhat predictable. The suspension containing low molecular weight material gave coatings that lost their opacity as soon as they were immersed in an aqueous solution. The suspension containing highly hydrolyzed grades, when coated without added gelatin, did not opaque on drying at 90°C but slowly became opaque over a period of days then stored in ambient air. The suspension containing the 98% hydrolyzed sample, when coated with added gelatin binder, opaqued when dried at 90°C. That containing the 100% hydrolyzed sample, under the same conditions, again did not opaque until a period of time had elapsed. The DTM samples containing the highly hydrolyzed grades retained their opacity well on processing as can be seen by referring to Table 1 in the discussion section of this report. The improved opacity shown by one of the samples after processing was due to the fact that the particular sample had not fully opaqued when it was tested and the aqueous treatment removed the residual cumene from capsules that had not emptied. Unfortunately, all of the coatings were found to have poor wet rub resistance.

#### Stoichiometric Preparations

In an attempt to consume all of the polyamines at the capsule-forming stage so that the microcapsule suspension would be compatible with Carboset XL-19, some preparations were carried out using a stoichiometric equivalent of terephthaloyl chloride. The ability of cumene containing dissolved polymers to solubilize more of the acid chloride than pure cumene was utilized to increase the concentration of terephthaloyl chloride. Instead of the normal 10% solution of acid chloride, a 16% solution was prepared in cumene saturated with polymethyl methacrylate. All other parameters of the preparation remained the same. The microcapsules formed had very thick walls and, as a result, coatings made from this capsule suspension did not opaque on drying at 90°C. Also, the amount of sodium carbonate present in the amine solution, was insufficient to neutralize all of the hydrochloric acid generated at the capsule-forming stage. A droplet of the microcapsule suspension added to Carboset XL-19 did not cause precipitation, which suggested that all of the polyamines had been consumed. Coatings of the suspension made with a #15 Meyer rod on Carboset XL-19 subcoated pieces of black polyester dried to a transparent condition at 90°C. They gave a white mark against a black background much the same as a dry DTM. When the coating was soaked in water, it became opaque and a mark then showed up as a black area against a pale white background. The wet rub resistance of the coating was fair. However, when the coating dried after being in contact with aqueous solutions it cracked to give an alligatored pattern. Coatings made with added gelatin to increase binder content displayed a similar behavior with the exception that they became opaque after several days storage in ambient atmosphere. (Coatings from the filtered preparation with no added binder have remained transparent for four months).

A modified preparation was carried out with an increased amount of cumene (returning the acid chloride content to 10%) and with the substitution of ammonium hydroxide for sodium carbonate in the aqueous amine phase. (Release of carbon dioxide had caused much foaming in the previous preparation). To 25 ml of cumene saturated with polymethyl methacrylate was added 2.0g of terephthaloyl chloride, and the mixture was heated until all was in solution. The solution was emulsified into 25g of 2.5% Gelvatol 20-90 solution in the usual manner. The emulsion was added to a stirred solution of 8ml of water containing 1.5g ammonium hydroxide, 0.5g ethylenediamine and 0.3g diethylenetriamine. Because of the increased amount of cumene present, the capsules formed were somewhat larger than those formed by the standard procedure. A droplet of the solution tested by addition to some Carbo-set XL-19 caused precipitation, which indicated that some polyamine was still present. Although the preparation was incompatible with the Carbo-set, the usual testing procedure was followed for evaluating DTM coatings from it. Coatings containing a total binder content of 6% retained opacity after processing and, while not adequate in wet rub resistance, did not rub off as easily as the average DTM coating.

A third stoichiometric preparation was carried out using tetrachloroethylene saturated with polystyrene as the organic phase and replacing the ammonium hydroxide with 1.1g of sodium carbonate. (Failure to consume all of the polyamines in the previous preparation was thought to be due to reaction of some of the acid chloride with ammonia). The microcapsule suspension formed caused only slight precipitation with Carbo-set XL-19 indicative of only a trace of remaining polyamine. The suspension was made up to 5.5% total binder content. Black matte polyester directly subcoated with gelatin was first coated with a 5.5% solution of formaldehyde in methanol, then with the suspension. The coating did not opaque on drying at 90°C but became opaque on standing for two days. Testing of the coating indicated that it had good wet rub resistance after processing, but not after just wetting with water. A scratch made while the coating was wet showed good contrast but, after the coating dried, the opacity loss was severe enough that the scratch could not be readily detected.

#### Waterproofing Agents

Two organosilicon preparations used in waterproofing applications, Dri-Film and 3-heptafluoroisopropoxypropyltrichlorosilane (3-hept) were incorporated into the cumene phase in an attempt to waterproof the capsule pores and prevent leakage of water into the capsules during processing. Since both contained hydrolyzable chlorines, the amount of sodium carbonate in the amine-carbonate solution would have had to be increased to compensate for the additional hydrochloric acid generated. Because this would have increased the evolution of carbon dioxide and caused excessive foaming, ammonium hydroxide was substituted for the sodium carbonate. For the Dri-Film preparation, 1.2g of terephthaloyl chloride and 1.0g of Dri-Film were added to 15 ml of cumene. When heating to 60°C failed to dissolve all of the acid chloride, 2g of cumene saturated with polymethyl methacrylate was added to aid in solubilizing the remainder. The cumene solution was then emulsified into 25 ml of 2.5% Gelvatol 20-90. The emulsion was added slowly to a stirred solution of 8 ml of

water containing 1.5 ml concentrated ammonium hydroxide, 0.4g ethylenediamine, and 0.3g diethylenetriamine. The microcapsules that formed were normal in appearance and the solution tested alkaline at the completion of the capsule-forming step. Coatings made from this preparation lost opacity on processing and had poor wet rub resistance.

For the 3-hept preparation 1.2g of terephthaloyl chloride and 1.2g of 3-hept were dissolved in 15 ml of cumene at 60°C. The cumene solution was emulsified into 25 ml of 2.5% Gelvatol 20-90 and the emulsion was added to 8 ml of water containing 1.0g concentrated ammonium hydroxide, 0.4g ethylenediamine and 0.3g diethylenetriamine. Capsule formation was accompanied by excessive clumping and the suspension was found to be acidic. Adjusted the pH to 6 by dropwise addition of concentrated ammonium hydroxide. This preparation was difficult to filter but coatings prepared from it had the best wet rub resistance, whether wet with plain water or after processing, of all of the coatings tested during the course of the program. Unfortunately they lost opacity totally on processing.

An attempt was made to counteract the loss of opacity by using cumene saturated with chlorosulfonated polyethylene in place of cumene in a preparation. The only other change made was an increase in the amount of ammonium hydroxide to 1.3g. After microcapsule formation was complete the suspension was still acidic. The filtration difficulty persisted. The coatings prepared retained their excellent wet rub resistance but still lost their opacity totally on processing.

#### Miscellaneous

Polyamide capsule walls formed by condensation of terephthaloyl chloride with ethylenediamine and diethylenetriamine are hydrophobic. In an attempt to increase their compatibility with the aqueous gelatin/PVA coating medium three preparations were made in which the amine component contained solubilizing groups. For two of them 1.25g of o- or p-sulphophenylhydrazine was used as the equivalent of 0.4g of ethylenediamine. For the third 0.45g of 2-[N,N-bis(2-aminoethyl)-amino]-ethanol was used as the equivalent of 0.3g diethylenetriamine. The behavior of these preparations was similar to that of the normal preparation; there was no indication of increased hydrophilic nature.

On an earlier contract during investigations of the dry DTM the substitution of hydrazine or phenylhydrazine for the usual polyamines gave rise to microcapsule coatings that were harder to scratch. Preparations were carried out with 0.35g of hydrazine, or 0.55g of phenylhydrazine used as the equivalent of 0.4g ethylenediamine. The phenylhydrazine preparation gave rise to coatings that retained opacity after processing but had poor wet rub resistance.

The influence of inorganic additives that might have crosslinking properties was evaluated at various stages in the encapsulation procedure. When the water used to dissolve the sodium carbonate and polyamines was replaced by an equal volume of Nyacol colloidal silica, Grade 215 (Nyanza) addition of the emulsified cumene phase



caused the solution to thicken badly. Diluting with twice its volume of water was required before the preparation could be completed. The presence of colloidal silica changed the properties of the microcapsule suspension. The capsules that formed were normal in appearance but, when the suspension was subjected to ultrasonic agitation to break up the clumps, the preparation thickened instead of thinning out. Coatings made from this formulation were very granular but had good opacity. The coating containing 4% binder was best from the standpoint of retention of opacity after processing and wet rub-resistance. However, when the force of the sink spray was directed on the coating there was some wash-off of material.

Nyacol colloidal titania solution (27g/l), when mixed with dilute gelatin solutions, caused immediate gelation. However, when 8.2g of the colloidal titania was added to 16.8g of 3.8% gelatin solution, the gel formed was loose enough to be stirred. When 15 ml of cumene containing 1.2g terephthaloyl chloride, 0.5g triphenyl phosphite and 0.3g Dow Corning 1108 fluid was emulsified into this gel with the aid of the ultrasonic probe, the emulsion became so thick that it would only tolerate 10 seconds of agitation at setting 4 instead of the usual 30. The emulsion had to be scraped into the stirred solution of 8 ml of water containing 0.8g sodium carbonate, 0.4g ethylenediamine and 0.3g diethylenetriamine. Capsule formation took place normally and the mixture never became viscous enough to stop the stirrer. This preparation also produced very grainy coatings. The coatings had both poor dry rub and wet rub characteristics.

Silane adhesion promoter A-1120 (Union Carbide) has dual functionality. It is a diamine and as such should be capable of substituting for ethylenediamine in a capsule preparation. It also contains three hydrolyzable groups on the silicon atom which give it properties similar to a silicate. Since the colloidal silica seemed to improve wet rub resistance two attempts were made to incorporate the silane into the capsule wall in the hope that hydrolysis at the silicon atom would help bond the capsules better to gelatin or polyvinyl alcohol. In the first attempt cumene saturated with chlorosulfonated polyethylene was used to dissolve the terephthaloyl chloride and the solution was emulsified into 2.5% Gelvatol 20-60. However, when the emulsion was added to the stirred amine-carbonate solution (with 1.5g of the A-1120 replacing 0.4g of ethylenediamine) the blend became very mushy and could not be stirred. The emulsion was mixed in with a glass rod and microcapsules were formed. Clumping was severe so the makeup gelatin was added before filtration was attempted. The addition of the gelatin made the suspension fluid enough that ultrasonic agitation could be applied to break up the clumps. The suspension could not be filtered. Some of it was coated directly on the black polyester. The coating was granular in appearance (rough surface) but would not wash off in water or in processing solutions. It could be rubbed off when wet but light rubbing did not affect it.

In the second preparation the chlorosulfonated polyethylene was eliminated and 1.2g of terephthaloyl chloride and 0.1g of sodium dioctyl sulfosuccinate were dissolved in 15 ml of cumene. The cumene was emulsified into 40 ml of 2.5% gelatin solution. The emulsion was poured slowly into a stirred solution of 8 ml of water containing 0.8g sodium carbonate, 1.5g A-1120 and 0.3g diethylenetriamine. All mixtures remained fluid throughout the preparation. The microcapsule suspension filtered

rapidly and coatings were made from it on a VMCA subcoating containing A-186 silane adhesion promoter. After drying at 90°C the coatings were primarily transparent. They had good wet rub resistance both when wet with water or with processing solutions. However, because of their lack of opacity, scratch marks were of low contrast and not readily detected.

#### COMPATIBILITY STUDIES

Treatment of the dyed black polyester to improve its wettability or the presence of a hydrophilic subcoating did not seem to reduce the tendency of the microcapsule coating to break up into gross patterns after it had been spread by the Meyer rod. A 5% gelatin solution, on the other hand, although showing large repellent areas on untreated black base, coated smoothly on the subcoated material. To determine the influence of free cumene on the coating properties of gelatin, 7.5 ml of cumene and 25g of 5% type 2403 gelatin solution were combined in a 50 ml beaker. The mixture was stirred with a magnetic stirrer and emulsified by agitating with the ultrasonic probe for 30 sec. on setting 4. A coating drawn from this milky emulsion on an S/MA subbed piece of black polyester with a #25 Meyer rod broke up into gross circular patterns of white (emulsion coated) and black (uncoated) areas. When dried at 90°C, the coated areas had a similar appearance to microcapsule coated base. Examination under the microscope indicated the presence of many circular voids where the cumene droplets had escaped.

The emulsion was divided into several 2 ml portions and various substances were added to try to overcome the effect of the cumene. In each case the addend was stirred into the emulsion with a glass rod while the emulsion was being warmed to aid dispersion. The coating was applied with a #25 Meyer rod and dried at 90°C. Addends included 2 drops of methanol, and 1 drop each of a number of wetting agents including Aerosol OT (anionic), the DuPont fluorosurfactant series of Zonyl FSA (anionic), FSB (amphoteric), FSC (cationic) and FSN (nonionic), 10% saponin solution, Photo-Flo, Alkanol B (anionic), Lomar D (anionic) and Benax 2A1 (anionic). With the exception of Photo-Flo which had a demulsifying effect, all of the substances reduced the size of the repellency spots. Methanol only had a slight effect which indicated that the approach of adding a water miscible co-solvent would probably not be profitable. The coating containing Aerosol OT dried perfectly smooth and transparent with no trace of repellency spots. All of the other coatings had some degree of opacity, appearing gray to white. The nonionic wetting agent, although it reduced the diameter of the repellency spots from the 10-15 mm range to the 1-2 mm range, still led to a coating that had a very high level of uncoated spots. The presence of the other Zonyl surfactants led to many small circular white raised areas in the coatings which were due to air bubbles produced on stirring the surfactants into the emulsion. Saponin, which at one time was the favored wetting agent for use with gelatin, was not as effective in reducing the diameter (3-4 mm) and frequency of the repellency spots. All of the coatings swelled when placed in water and the opaque ones lost all their opacity on drying.

The ability of the Aerosol OT to control free organic solvent was confirmed with two other substances that could possibly be present as contaminants, methylene chloride (used to put down some of the subcoatings) and tetrachloroethylene (used for making microcapsules heavier than water). An emulsion of 15 ml methylene chloride

in 25 ml of 5% gelatin (type 2403) solution was tested as above. Again the sample with added Aerosol OT gave a transparent, repellency-free coating and the nonionic Zonyl FSN gave a coating with a high frequency of very small repellencies. Similarly an emulsion of 15 ml of tetrachloroethylene in 25 ml of 5% gelatin solution gave a smooth, transparent coating in the presence of Aerosol OT while all coatings containing the Zonyl series of surfactants were opaque on drying. In this case the coatings were made directly on the black matte polyester (no subcoating). The coating containing the Aerosol OT was the only one that could not be pulled from the substrate with Scotch tape. It could also be cycled through photographic processing solutions without loosening from the base.

#### PREPARATION AND COATING OF DRY DTM

Three batches of microcapsules were prepared by the following procedure: In 170g of tetrachloroethylene 10g of terephthaloyl chloride was dissolved by warming the mixture to 60°C. The solution was emulsified into 400 ml of water containing 1.5% type 2403 gelatin and 1% Gelvatol 20-60 by the procedure described for the wet DTM preparations. Then 70 ml of water containing 6.4g sodium carbonate, 3.2g ethylenediamine and 2.4g diethylenetriamine was added rapidly to the stirred emulsion. Stirring was continued for 5 minutes to ensure the completion of capsule formation.

The three batches were combined and the 1800 ml of microcapsule suspension was warmed and stirred with 1200 ml of 10% Type 2403 gelatin solution. The mixture was filtered through a 50 $\mu$ m rated viscose filter to remove particulate matter. It was collected in a 4 l reservoir which was then placed under the feed line of the first coating station on the multihead coater. The coating head was fitted with a 5 mil shim and the microcapsule solution was forced through the head by means of a Zenith pump onto a traveling 7-inch web of flashed, processed SO-192. Approximately 900 ft. of substrate was coated.

This procedure was repeated several times and the resulting webs of dry DTM were examined. Sections with a high frequency of defects were cut out and the remaining material was spliced together and slit to 6.6 inch width. Approximately 2500 to 3000 ft of dry DTM was delivered.

#### IV PROPERTIES OF THE DTM COATINGS

Although the work on Contract No. F33615-76-C-1179 did not succeed in its final aim of providing a wet DTM on a dyed polyester substrate, coated versions of both the dry and wet DTMs have been prepared and tested on Contract No. F33615-74-C-1151 and in the earlier phase of this contract. The general properties of the coatings obtained are described here. The section on conclusions and recommendations will describe the work needed to provide each DTM as a standard material for testing purposes.



## DRY DTM

The DTM provided for dry applications was a coating of tetrachloroethylene-filled microcapsules on a flashed, processed web of SO-192. The microcapsules were essentially transparent, which gave the material an overall black appearance; nonuniformities in the coating were lost in the black background. This DTM was pressure sensitive and had to be handled with care to avoid breaking some of the capsules and creating some white background. Despite its high degree of sensitivity, it could stand quite a bit of handling without destroying its ability to record scratches and abrasions. (Generalized pressure creates a low contrast white background against which the higher contrast scratch can still be seen). It has been spooled, unspooled, and run through a slit with minimal damage evident to the eye.

A scratch tester consisting of a weighted ballpoint from a ballpoint pen was used for rough testing. This tester weighted with 2g produced a barely visible scratch on a sample of cleared Estar-based film. On the dry DTM a 1g weight produced a clearly visible scratch. As the weight was increased the scratch produced increased in both width and contrast. The dry DTM is capable of indicating the amount of stress placed on a given area because the coating consists of many layers of microcapsules. A light scratch penetrating only slightly breaks less capsules than a heavy scratch that penetrates more deeply.

The dry DTM, as furnished, is not suitable for wet applications since the microcapsules tend to wash from the substrate on contact with solutions and the coating also tends to lose its transparency. The most serious drawback of the material furnished as a sample was its limited shelf life. The microcapsules are somewhat porous and the solvent in them is gradually lost. When the major portion of the solvent has disappeared the capsule coating becomes opaque and scratches can no longer produce sufficient contrast for clear delineation of the affected area. The DTM may be too sensitive for some applications because it will give a detectable response at levels well below those where film will show detectable damage. However, the sensitivity can be varied by relatively minor changes in formulation.

## WET DTM

Although a successful version of the wet DTM on dyed polyester was not prepared, the wet DTM on a flashed, processed SO-192 substrate could potentially be hardened to eliminate the shortcomings found on the sample submitted. The DTM for wet applications, because it contains light scattering centers and appears white against a black background, presents a more difficult coating problem than the dry DTM. Any variations in coating thickness or any coating imperfections are readily visible. However, once coated, the wet DTM has better handling characteristics. The white coating, when dry, is not pressure sensitive and the DTM can be handled just like regular film without danger of damage. A weight of approximately 20g had to be applied to the scratch tester to give a visible mark on the approval sample. However, the disturbance caused by a stylus weighted with 5 or 10g became visible

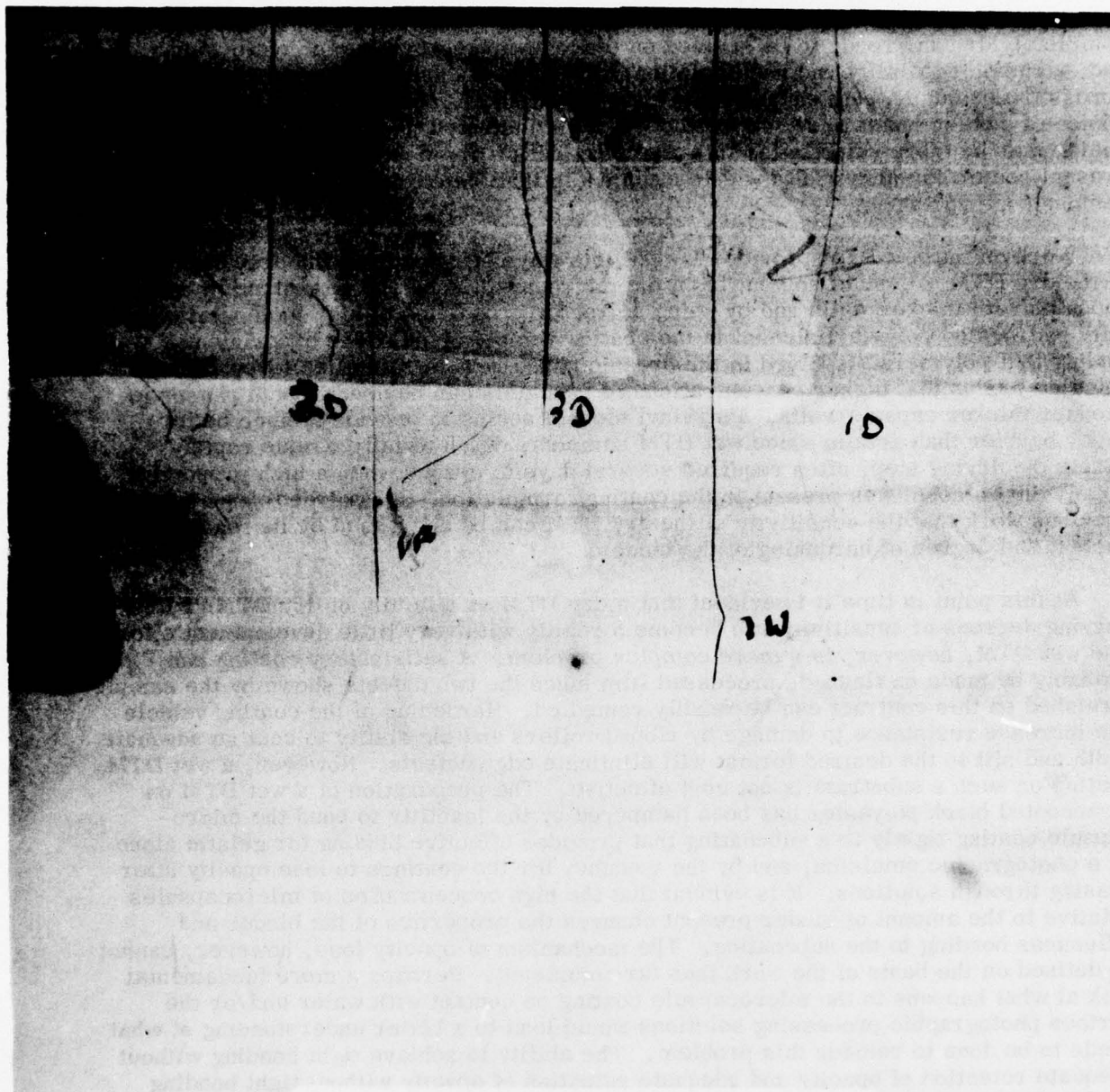
when the DTM contacted an aqueous solution. Water has a definite softening effect on the DTM and when it is wet a detectable mark can be produced with a 1g weight on the stylus. Solutions with a high salt content, such as developer solutions, do not soften the coating as much. A hardening fixer hardens the DTM sufficiently that it can be subsequently washed without increasing its scratch sensitivity. Because the wet DTM softens, any object scratching it penetrates the coating to the base. Thus there is no correlation between the scratch profile and the severity of the scratch-causing defect.

Material cut from the coating delivered to the customer was tested to determine its general properties. The tests were performed three hours after the DTM was prepared. First a sample was agitated in contact with developer (D-19) for eight minutes. The back of the substrate was wiped and the sample was tested with the scratch tester. One, two, and three gram weights on the stylus produced a graded series of scratches. The 1g scratch was barely visible with the 3g scratch being wider and more readily seen. The sample was then rinsed in water for 1 min and, after the back of the substrate was again wiped, was retested. A 1g weight on the stylus produced a scratch equivalent to that produced by the 2g weight on the previous test indicating that the coating softened even more in water than it did in developer. The sample was then fixed (Kodak Acid Fix), the back of the substrate was wiped, and the influence of a 1g scratch was again determined. Fixing hardened the coating to some extent as the 1g scratch was barely visible. The test results are illustrated in Figure 2.

To determine whether the DTM would withstand a spray rinse the hot water was turned on in the laboratory sink and the spray unit of the sink was used to direct the water onto a sample of the coating. There was no evidence of wash-off during this procedure. During a conference with technical representatives of the customer a sample of the wet DTM was immersed in a cup of water and scratched several times with various objects. It was then set aside and forgotten until the end of the day. The coating remained intact after approximately five hours of direct contact with water.

## V CONCLUSIONS AND RECOMMENDATIONS

The present status in the development of degradation test materials can best be summarized by detailing what needs to be done in the case of both wet and dry materials to provide a viable product. The dry DTM, which has received little attention since the submission of the initial sample rolls in 1975, requires relatively minor alterations to be suitable for testing apparatus in which film must be transported. The transition from a flashed, processed film substrate to a dyed black polyester substrate should not be difficult since the subcoatings developed on this contract are all capable of holding the DTM layer under conditions where immersion in water is not required. The transition from the old coating machine to the one set up on this program should be beneficial. In the old coater the coated side of the substrate had to pass over undercut rollers while it was still wet. Any loss in tension or development of curl allowed the wet coating to touch the undercut area and smear. On the present coater only the back side of the substrate comes in contact with the rollers until the coating is



**Figure 2** Sample of Wet DTM Scratch-Tested during Processing

Vertical scratches at top show the effect of the stylus weighted with, from left to right:

2D - 2g, after development

1F - 1g, after fixation

3D - 3g, after development

1W - 1g, after wash following development

1D - 1g, after development



completely dry and ready to be spooled on the take-up reel. The old coater only had extrusion capability, and accumulation of bubbles or particulate matter anywhere across the extrusion path caused streaks in the coating. The present coater has a choice of coating heads and tests on the wet DTM indicated that the reverse roll coater may be more suitable for this type of coating. As mentioned before, the present coater can also coat a wide enough width that the edges can be slit away to remove edge variation.

Work on the wet DTM provided insight into ways of remedying the drawbacks of the dry DTM. Loss of solvent from the microcapsules can be restricted by making capsules with thicker walls and by using a greater proportion of high molecular weight, fully hydrolyzed polyvinyl alcohol in the coating vehicle blend. The experimental finding that polymers dissolved in the organic phase help to solubilize terephthaloyl chloride means that higher concentrations of reactants can be used in both phases to produce thicker capsule walls. Polyvinyl alcohol seems to provide a much better vapor barrier than gelatin since wet DTM samples, which usually opaque rapidly during the drying step, often required several days to opaque when a high proportion of polyvinyl alcohol was present in the coating formulation. It is already known from previous work that the sensitivity of the dry DTM can be decreased by increasing the content and degree of hardening of the binder.

At this point in time it is evident that a dry DTM or a family of dry DTMs with varying degrees of sensitivity can become a reality with very little development effort. The wet DTM, however, is a more complex problem. A satisfactory coating can probably be made on flashed, processed film since the two defects shown by the sample furnished on this contract can be readily remedied. Hardening of the coating vehicle can increase resistance to damage by ribbed rollers and the ability to coat an adequate width and slit to the desired format will eliminate edge defects. However, a wet DTM coating on such a substrate is not cost effective. The preparation of a wet DTM on a subcoated black polyester has been hampered by the inability to bond the microcapsule coating tightly to a subcoating that provides effective binding for gelatin alone or a photographic emulsion, and by the tendency for the coatings to lose opacity after passing through solutions. It is evident that the high concentration of microcapsules relative to the amount of binder present changes the properties of the binder and influences bonding to the subcoating. The mechanism of opacity loss, however, cannot be defined on the basis of the work thus far completed. Perhaps a more fundamental look at what happens to the microcapsule coating on contact with water and/or the various photographic processing solutions would lead to a better understanding of what needs to be done to remedy this problem. The ability to achieve tight bonding without adequate retention of opacity and adequate retention of opacity without tight bonding from individual formulations suggests that the problems are not insurmountable.